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THE REACTION OF NITROUS ANHYDRIDE WITH ETHYL MALONATE.

BY RICHARD SYDNEY CURTISS.

Many years ago Conrad and Bischoff[1] studied the reaction of these two substances in the presence of sodium ethylate. They passed the red gases, formed by the action of nitric acid and arsenious anhydride, into ethyl malonate, dissolved in alcohol containing 1 atom of sodium. When the solution became saturated with the gas and showed only a slight alkaline reaction, they precipitated an oily product by diluting it with water. They attempted to purify this oil by washing it with water and subjecting it to fractional distillation in a vacuum. This process decomposed the substance. They then simply washed the oil with water and dried it. The analytical results correspond well with the formula $HON : C(CO_2C_2H_5)_2$, that of ethyl isonitrosomalonate.

They found the yield of oil variable and never over 50 per cent of the ethyl malonate used. I have recently had occasion to use the ketonic ester, ethyl oxomalonate, $OC(CO_2C_2H_5)_2$, and the related crystalline body, ethyl dihydroxymalonate, $(HO)_2C(CO_2C_2H_5)_2$, in considerable quantities, and have found the older methods of preparation described by Beilstein[1] very costly in material, time and labor. The following procedure overcomes these difficulties and gives a yield of 90–95 per cent of the pure esters, with very little expenditure of time or material. It is also superior to the methods described more recently by Bouveault and Wahl[2] and Schmidt.[3] It is somewhat similar to the above process, whereby Conrad and Bischoff obtained ethyl isonitrosomalonate, no sodium ethylate is used, however.

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[1] Ann. Chem. (Liebig), **209**, 211.

The so-called nitrous anhydride was generated by the action of warm nitric acid, sp. gr. 1.42, on arsenious oxide, conducted through a flask to condense moisture and, without drying, passed in a rapid stream into 50 grams of ethyl malonate, at 0°, the latter substance being contained in a distilling flask, immersed in a freezing mixture. The gas is extremely soluble in the liquid. Very little heat is generated in the reaction. A rapid stream of the gas is completely absorbed for three quarters of an hour. The operation was then stopped, 58 grams of gas had been absorbed. The pale blue color first formed rapidly changes to a dark green, almost opaque at the last. The flask and contents are allowed to remain in the ice mixture for several hours at 0°, then to slowly assume the temperature of the room, and remain thus for nearly 2 days, at 23°–28°. As it warms, red gases are slowly evolved; the loss in weight, in 18 hours, is 11 grams, and after 40 hours, 14 grams. The total weight of the crude green oil at this stage is 94 grams. This green oil consists chiefly of the anhydrous and hydrated mesoxalic esters, together with small amounts of oxalic acid and ester, acetic acid and ester, and ethyl isonitrosomalonate.

At this point the process may be varied in 3 ways, dependent on the product wanted, whether ethyl oxomalonate (1), ethyl dihydroxymalonate (2), or the free mesoxalic acid (3).

(1) If the keto ester, ethyl oxomalonate, $OC(COOC_2H_5)_2$,

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[1] "Beilstein's Handb. d. org. Chem." I., 788; Sup. I., 371.

[2] Compt. rend., **137**, 196.

[3] *Ibid.*, **140**, 1400.

is desired, the process of vacuum distillation is used on the crude oil. As the pressure is reduced the excess of red gases passes off, leaving in the flask a straw colored liquid, which distils almost entirely without destructive decomposition or darkening, leaving only 1–2 grams of thick, yellow syrup as residue. The first fraction (10 grams), passing over from 52° (70 mm.) to 70° (45 mm.) contains a little water, acetic acid and some esters. Then the distillate ceases, the temperature rises regularly from 70° to about 120°; around 125° (70 mm.) a thick, amber-colored oil distils over, together with a little water. This mixture crystallizes in the receiving tube and consists of ethyl dihydroxymalonate. It is followed by the anhydrous ester, ethyl oxomalonate. This substance is the main product of the distillation. It passes over at 126°–133° (42 mm.–50 mm.), (uncorr.) and weighs 55–60 grams.

(2) If the crystallized ethyl dihydroxymalonate,

$$(HO)_2C(CO_2C_2H_5)_2,$$

is desired it may be readily obtained in two ways:

(*a*) The requisite quantity of water may be added to the above distillate of pure ethyl oxomalonate. This causes the temperature to rise to 45°; it remains there while the liquid changes to a solid, crystalline mass of beautiful white plates. This is pure ethyl dihydroxymalonate, melting at 57°.

(*b*) The original crude, green oil, saturated with nitrous anhydride, may be poured into a large crystallizing dish and left exposed to the air. It loses thus its excess of absorbed gases, while it takes on atmospheric moisture, rising in temperature thereby, and slowly passes into a crystalline mass. This also, when filtered with the aid of a pump and well washed with carbon bisulphide, is practically pure ethyl dihydroxymalonate. It was recrystallized from ether, dried quickly in a vacuum over sulphuric acid and analyzed:

	Calculated for $(HO)_2C(CO_2C_2H_5)_2$.	Found.
C	43.75	44.19
H	6.25	6.58

The carbon appears somewhat high, owing to the fact that this substance loses water in a desiccator and changes to the ketonic ester, ethyl oxomalonate.

(3) If the free mesoxalic acid $(HO)_2C(COOH)_2$ is desired, it can be readily made from the crude oil as follows: Twenty-five cc. of this oil is extracted with 10 cc. of cold water, which dissolves its own weight of soluble products. A second extraction is made, but removes little soluble matter. This aqueous extract is placed in a crystallizing dish and evaporated in a vacuum desiccator, over sulphuric acid. A dry, crystalline mass of mesoxalic acid remains. This substance deliquesces in the open air, changing into a thick, colorless syrup. Placed again over sulphuric acid, it recrystallizes in the forms characteristic of dihydroxymalonic acid. Its identity is further shown by its melting-point, 115°-116°, its ability to form insoluble calcium, barium and silver salts and, when mixed with phenylhydrazine and acetic acid, it yields a yellow body, which, recrystallized from alcohol, agrees in its melting point, 160°, and other characteristics with the phenyl hydrazone of dihydroxymalonic acid.

There is much that is misleading in the literature concerning ethyl dihydroxymalonate. The following properties of this substance have been noticed, in addition to those recorded by Beilstein:

The statement is made by this author[1] that ethyl dihydroxymalonate is insoluble in water. Conrad and Brückner[2] attribute this erroneous statement to W. Petrieff, and refer to his papers.[3] No assertion whatever concerning the solubility of this substance is there made.

On the contrary, ethyl dihydroxymalonate is extremely soluble in water; 1 gram, at 22°, dissolves 1.3 grams of the substance, accompanied with a slight lowering of the temperature of the solution. One gram of ethyl malonate dissolves 0.6 gram of the crystals, a fact which has a decided bearing on the above method of separating it by crystallization. One cc. of benzene, at 22°, dissolves 0.2 grams of the ester. It is also easily soluble in ether, acetone, chloroform and absolute alcohol. It is slightly soluble in ligroin and insoluble in carbon bisulphide. Pure ethyl dihydroxymalonate is volatile in air at ordinary temperatures, and especially so in a vacuum. If a film of it be left on a watch-glass, in a current of air, it disappears entirely in 24 hours. It loses water in a desiccator, thereby changing to an oil, but it is quite stable in moist air at ordinary temperatures, and can be thus kept for months without decomposition. Only in an impure form does it slowly soften and liquefy. It can be distilled under reduced pressure (40–50 mm.) without any darkening in color, or any marked decomposition other than the loss of a molecule of water and the formation of the ketone form of the ester.

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[1] "Handb. der Organ. Chem.," I., 788.

[2] Ber. d. chem. Ges., 24, 3000.

[3] *Ibid.*, 8, 730; 11, 415.

In a note[1] on the subject of this paper the more recently discovered reactions which produce mesoxalic esters were discussed and, among others, that of Bouveault and Wahl,[2] who produced it by the action of nitric oxide upon ethyl isonitrosomalonate. They had also noticed that the latter ester was formed by the action of nitric oxide upon ethyl malonate.

At the time that the above note[1] was printed, Schmidt,[3] carrying out the ideas of Bouveault, presented to the French Academy a paper describing a process for making ethyl oxomalonate, by a combination of these two reactions. Nine hundred grams of dry sodium nitrite were mixed with 3000 grams of sulphuric acid, below 0°. The resulting nitrosylsulphuric acid was decomposed with water, and the nitric oxide passed into a mixture of 200 grams of ethyl malonate, in acetic anhydride. The process was continuous for several days, then the liquid was distilled in a vacuum. A 65 per cent yield of a product was obtained, which had a boiling point of 95°–130° (15–25 mm.) and was called "ethyl mesoxalate." As this substance, ethyl oxomalonate, boils constantly at 126°–127° (45 mm.) (uncorr.), the above product, with a variation of boiling point of about 25° at constant pressure, must consist largely of other substances. The yield of pure ester is not given, nor that of the crystals of ethyl dihydroxymalonate, which form in the oil.

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[1] THIS JOURNAL, 33, 603.

[2] Compt. rend., 137, 196.

[3] *Ibid.*, 140, 1400.

The process described in the present paper requires but 2-3 hours of the chemist's time, and gives a yield, on the ethyl malonate used, of 90 per cent or more of pure ethyl dihydroxymalonate (m. p. 57°-58°). If desired, the yield can be raised above 95 per cent by repeating the process on the small amount of oil filtered off from the crystalline product.

The action of nitrous anhydride on ethyl malonate gives other products, in quantities varying widely with the conditions of temperature, moisture, degree of saturation with the gas and time of reaction.

Experiments in which a little water was added to the ethyl malonate and the gas then passed at 0° and allowed to stand a few days, gave a considerable quantity of acetic acid and ester. Oxalic acid crystallized out from the aqueous liquid at the bottom of the flask. The effect was, therefore, saponification of the malonic ester, loss of carbon dioxide and decomposition of ethyl mesoxalate, with formation of oxalic acid.

This change of ethyl oxomalonate to oxalic acid takes place slowly in the mixture, even in the absence of any considerable quantity of water, as shown by the following experiment: A loosely covered cylinder containing 21 cc. of ethyl malonate, was saturated with the gas and placed in the window in the sunlight. Crystals of oxalic acid began to deposit within a week. It was allowed to stand there 8 months and slowly lost gas during the entire time. The volume of oil decreased 50 per cent and was filled to the surface with balls of needle-shaped crystals. The various tests applied showed these to be oxalic acid.

If the ethyl malonate is only partially saturated with nitrous anhydride, ethyl isonitrosomalonate is present in considerable quantity, just as Conrad and Bischoff[1] discovered, when working with ethyl malonate in the presence of sodium and alcohol. Twenty-five grams of nitrous anhydride were dissolved in 50 grams of ethyl malonate, by passing the gas into the ester at 0°, for one-half hour. It then stood 32 hours at the ordinary temperature. The initial blue color of the oil had changed to a pale, greenish yellow, and its weight was now reduced to 65 grams. Further exposure to the air caused but slight loss in weight. In a short time 17 grams of crystals of ethyl dihydroxymalonate were deposited. Twenty-eight grams of the mother liquor from these crystals were mixed with an equal volume of ether and washed with a few cc. of cold water, then with a saturated solution of sodium carbonate to alkaline reaction. The excess of alkali was removed entirely by water. The oil (A) which remained, after drying with calcium chloride and evaporating off the ether in a vacuum at 40°, was pale green, weighed 29 grams and had a fragrant, though rather pungent odor, resembling that of brominated fatty esters. It was slightly acid to litmus. This oil appears to be chiefly ethyl isonitrosomalonate.

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[1] Ann. Chem. (Liebig), 209, 211.

This oil, 11.35 grams, was treated with 12.5 cc. of alcohol (96 per cent), which contained 1 mol. of potassium hydroxide. The alkali was added slowly and the temperature kept down to —10°. A yellow salt precipitated at once and was quite pure. If precipitated at ordinary temperatures gases are evolved and the product is impure. After standing 15 minutes, the cold mixture was filtered by means of a pump, washed well with alcohol and then with ether; 3.85 grams of salt were thus obtained. The yield is larger if absolute alcohol is used, as it is quite soluble in 95 per cent alcohol and especially so in water. The salt was twice recrystallized from hot, 95 per cent alcohol. It separates out on cooling in long, greenish-yellow needles. After drying in a vacuum, over sulphuric acid, it was analyzed. Potassium was determined as sulphate.

	Calculated for $KON:C(CO_2C_2H_5)_2$.	Found. I.	Found. II.
K	17.19	17.72	17.62

The salt dissolves easily in cold water, giving a yellow solution; it is fairly soluble in hot alcohol, slightly soluble in acetic ester, but insoluble in ligroin, chloroform and carbon bisulphide. Silver nitrate precipitates from its aqueous solution a beautiful yellow silver salt, which soon darkens in the light. Copper acetate gives a flocculent precipitate, soluble on dilution with water.

The potassium salt, placed in a melting point tube, in a bath at 185°, slowly darkens in color; heated rapidly it contracts and decomposes, with frothing, at 195°–200°. If, however, the dry salt be heated carefully in a test tube it reddens on the edges and suddenly explodes, with a flash of purple flame.

Conrad and Bischoff[1] confirm Baeyer's[2] observation that isonitrosomalonic acid, in aqueous solution, is decomposed at 40°, giving hydrocyanic acid, carbon dioxide and water.

I have been unable to obtain any test for hydrocyanic acid from the saponified ester, or from the products of the explosions of its potassium salt.

Attempts to make a sodium salt by the action of a 40 per cent aqueous solution of sodium hydroxide on a concentrated, ethereal solution of the oil (A) gave no precipitate, owing to the great solubility of this salt. On evaporating the solutions over sulphuric acid, however, a canary-yellow salt slowly crystallized out. It was not further purified. Neither could this salt be precipitated by the use of sodium hydroxide, dissolved in absolute alcohol.

Concentrated, aqueous ammonium hydroxide placed on the oil (A) gives a yellow solution, which, on evaporation in the air, deposits yellow crystals in the form of needles. This salt is unstable and soon turns red. Aniline reacts with the oil, giving a product which crystallizes in needle forms and is slightly soluble in alcohol and ligroin.

By neutralizing the sodium carbonate solution, which had been used in washing and purifying the above oil (A), with hydrochloric acid, 6 grams of a yellow acid oil were obtained. This was taken up in ether, the ether evaporated and the residual oil dried over sulphuric acid and solid potassium hydroxide. During the process of desiccation the alkali is coated bright yellow by some volatile substance.

A concentrated potassium hydroxide solution precipitates this oil, almost completely, in the form of a yellow potassium salt. A slight ammoniacal smell is apparent and the gas given off turns red litmus paper blue. The oil also forms a green copper salt with copper acetate solution. It was not further studied, but was assumed to be ethyl isonitrosomalonate.

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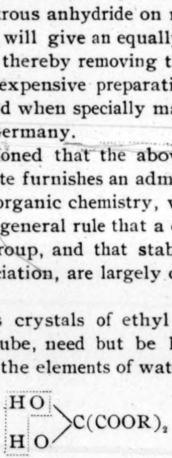
[1] Ann. Chem. (Liebig), 209, 211.

[2] *Ibid.*, 131, 293.

The reaction of nitrous anhydride on methyl malonate will be studied to see if it will give an equally satisfactory yield of methyl oxomalonate, thereby removing these substances from the list of rare and expensive preparations, which, hitherto, could only be procured when specially made to order by Kahlbaum and others in Germany.

It might be mentioned that the above method of making ethyl hydroxymalonate furnishes an admirable experiment for a laboratory class in organic chemistry, while illustrating the rare exception to the general rule that a carbon atom can hold but one hydroxyl group, and that stability of the molecule, dissociation and association, are largely questions of temperature.

The pure, colorless crystals of ethyl dihydroxymalonate, placed in a dry test tube, need but be heated to their melting point, 57°, when the elements of water dissociate,



$$\begin{matrix}HO\\HO\end{matrix}>C(COOR)_2$$

which fact becomes at once apparent as the drops of water condense in the upper, cold part of the test tube. There is a very marked change from the thin, colorless liquid first formed, on melting, to a green oil, ethyl oxomalonate, which remains at the bottom of the tube. If, now, the test tube be cooled, closed with a rubber stopper and tilted so that the two liquids come in contact, they reunite, there is an immediate loss of the green color, the temperature rises sharply and, on touching the colorless syrup on the sides with a glass rod, a remarkably beautiful and rapid crystallization starts and passes throughout the whole inner surface of the tube, yielding again the original crystalline mass. This experiment can be rapidly repeated many times with the same sample of substance.

The preparation also furnishes an interesting example of a ketonic ester in its reaction with aniline, with which it readily yields ethyl dianilinomalonate, $(C_6H_5NH)_2C(COOR)_2$, a substance crystallizing in beautiful rosettes of colorless needles.

In studying the action of phenylhydrazine on ethyl oxomalonate it has been noticed that it does not give the expected yellow crystalline phenylhydrazon as does the free acid, and also the acid ester, but yields an amber-colored oil which has *acid* properties.

A canary-yellow potassium salt has been made from this oil by treatment with alcoholic potassium hydroxide. This salt is stable in dry air but is dissociated by water, yielding the original acid oil. These reactions are being investigated.

URBANA, ILL.,
Feb. 28, 1906.

FURTHER INVESTIGATIONS OF THE TWO CHLORIDES OF ORTHOSULPHOBENZOIC ACID.[1]

BY PHILIP H. COBB.

The earlier investigations of the two isomeric chlorides of orthosulphobenzoic acid have left a number of points unsettled and it was in the hope of clearing up some of these that, at the suggestion of President Remsen, I undertook the work, an account of which is given in this article.

I. The Action of Hydrochloric Acid on Organic Anhydrides.

The action of alcohols on the low-melting chloride, in the cold, has been shown to consist in the formation of symmetrical ester chlorides, a fact which, taken by itself, would be a strong argument for the symmetrical structure of the chloride. In the light of the other evidence, however, it is plain that this reaction is not decisive, and in view of the fact that all of the distinguishing reactions show that the low-melting chloride is unsymmetrical, there must be some other explanation for the peculiar action of alcohol. It is always possible to assume a molecular rearrangement, but a more satisfactory hypothesis was suggested by Remsen.[1] The suggestion is this: When ethyl alcohol is allowed to act upon the low-melting chloride, the first step in the reaction would naturallybe the substitution of two ethoxy groups for the chlorine atoms, thus:

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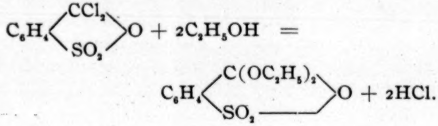
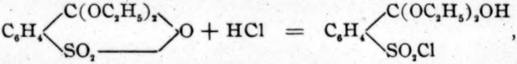
[1] From the author's dissertation submitted June, 1905, to the Board of University Studies of the Johns Hopkins University, in conformity with the requirements for the degree of Doctor of Philosophy.



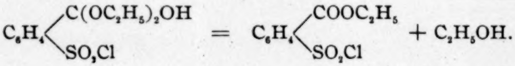
$$C_6H_4\left\langle\begin{array}{l}CCl_2\\SO_2\end{array}\right\rangle O + 2C_2H_5OH = C_6H_4\left\langle\begin{array}{l}C(OC_2H_5)_2\\SO_2\end{array}\right\rangle O + 2HCl.$$

The anhydride might then take up hydrochloric acid,



$$C_6H_4\left\langle\begin{array}{l}C(OC_2H_5)_2\\SO_2\end{array}\right\rangle O + HCl = C_6H_4\left\langle\begin{array}{l}C(OC_2H_5)_2OH\\SO_2Cl\end{array}\right. ,$$

and the product thus formed would lose alcohol and pass into the ester chloride:



$$C_6H_4\left\langle\begin{array}{l}C(OC_2H_5)_2OH\\SO_2Cl\end{array}\right. = C_6H_4\left\langle\begin{array}{l}COOC_2H_5\\SO_2Cl\end{array}\right. + C_2H_5OH.$$

In order to test this view experimentally, the action of dry hydrochloric acid on various organic anhydrides was tried. Experiments of this kind have already been made with acetic,[2] benzoic,[3] benzoic-acetic[4] and some other acids, but no experiments with the anhydrides of dibasic acids or inner anhydrides have been recorded. It appears that the anhydrides of monobasic acids react readily with dry hydrochloric acid. Attention was now turned to the inner anhydrides.

From the experiments performed it is evident that the anhydrides of the dibasic acids studied do not react with dry hydrochloric acid, while those of monobasic acids are easily attacked. Therefore the formation of symmetrical ester chlorides, by the action of alcohol on the low-melting chloride, does not seem to be dependent upon the presence of hydrochloric acid. The formation of symmetrical esters by the action of sodium ethylate upon the low-melting chloride also seems to furnish an argument against this explanation.

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[1] This Journal, **30**, 247.

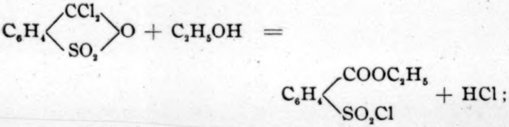
[2] H. Gal: Ann. Chim. Phys., [3], **66**, 187.

[3] Mosling: Ann. Chem. (Liebig), **118**, 303.

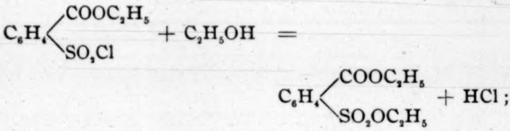
[4] Green: Bull. Soc. Chim., **33**, 426.

II. The Action of Alcohols and Alcoholates on the Chlorides.

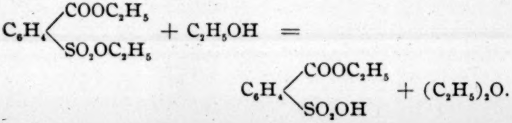
The action of alcohols upon the chlorides has been previously studied in this laboratory,[1] as well as elsewhere,[2] and it has been shown that the first products formed are ester chlorides which, upon further action of the alcohol, are transformed into the ester acids:

I.


$$C_6H_4\left\langle\begin{matrix}CCl_2\\SO_2\end{matrix}\right\rangle O + C_2H_5OH = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix}\right. + HCl;$$

II.


$$C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2Cl\end{matrix}\right. + C_2H_5OH = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2OC_2H_5\end{matrix}\right. + HCl;$$

III.


$$C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2OC_2H_5\end{matrix}\right. + C_2H_5OH = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2OH\end{matrix}\right. + (C_2H_5)_2O.$$

With the low-melting chloride the ester chloride is easily formed, while its isomer is only slowly attacked by cold alcohol.

The work along this line was continued by R. M. Bird,[3] who studied the action of the alcoholates as well. A brief summary of his results is as follows: The low-melting chloride, when dissolved in cold methyl alcohol, passed into the orthosulphone chloride and methyl benzoate. Upon evaporating the solution the substance separated in small, diamond-shaped crystals which melted at 57°–58° (corr.). They were soluble in alcohol and ether, but insoluble in water. Cold dilute sodium hydroxide did not affect the substance, but upon boiling it dissolved and chlorine was removed.

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[1] Remsen and Dohme; THIS JOURNAL, 11, 341. Remsen and Karslake: *Ibid.*, 18, 825.

[2] List and Stein: Ber. d. chem. Ges., 31, 1659.

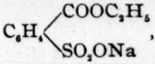
[3] THIS JOURNAL, 30, 247.

When the low-melting chloride was dissolved in methyl alcohol and the alcohol immediately boiled off, the orthosulphonic acid of methyl benzoate was obtained. Another product of this reaction was an oil which was shown to contain chlorine, and to it was assigned the formula of the orthosulphone chloride of methyl benzoate above described. It is, however, not stated that the oil became crystalline.

The orthosulphone chloride of ethyl benzoate was obtained by treating the dry, low-melting chloride with an alcoholic solution of sodium ethylate, until no more sodium chloride was precipitated. Upon extraction with ether and evaporation of the solvents, an oil remained which was insoluble in water, but soluble in alcohol and ether. When boiled with water it was hydrolyzed to an acid and hydrochloric acid was liberated. Treament with ammonia yielded the orthosulphone amide of ethyl benzoate.

What was, apparently, the same oil was obtained by treating an alcoholic solution of sodium ethylate with an ethereal solution of the low-melting chloride. As a by-product of this reaction another oil was obtained which answered the description of the diethyl ester of orthosulphobenzoic acid obtained by Remsen and Dohme.[1] It was soluble in water, alcohol and ether, and contained no chlorine.

By this same treatment and 2 hours' standing before examining the products, the sodium salt of the formula,



$$C_6H_4\begin{cases}COOC_2H_5\\SO_2ONa\end{cases},$$

was formed.

A slightly warm solution of 1.070 grams of sodium ethylate, in absolute alcohol, was gradually added to 1.996 grams of the low-melting chloride, in ethereal solution. The reaction progressed until one-half of the ethylate had been added, when it suddenly stopped and could be induced to go no further. The resulting product was an oil. With dry ammonia, crystals were produced which melted at 225°–226°. They were acid toward litmus and potassium carbonate. The crystals gave a product with a sweet taste when boiled with concentrated ammonia, as also did the oil when treated in the same manner. Upon boiling the oil with water it was hydrolyzed to an acid. No formula was assigned to the substance.

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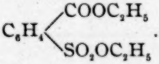
[1] This Journal, 11, 332.

An excess of ethyl alcohol was added to the low-melting chloride and boiled for 35 minutes. There resulted nothing but a neutral oil, which was soluble in water, alcohol and ether ; it contained no chlorine. Upon boiling with sodium hydroxide, ethyl alcohol was formed. The formula assigned was that of the diethyl ester,



$$C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases}.$$

None of the compounds above described, with the exception of the orthosulphone chloride of methyl benzoate and the sodium salt of ethyl orthosulphobenzoate, were analyzed. Certain considerations made it seem well to repeat the work :

1. The formation of ester chlorides by the action of sodium ethylate on the chlorides, and the impossibility of causing the reaction to go further.

2. The solubility of the so-called diethyl esters in water.

3. The production of a substance of acid reaction by boiling with ammonia.

4. The impossibility of obtaining the ester of a sulphonic acid by boiling its chloride with alcohol. Sulphonic acid esters are saponified by this process.

Action of Methyl Alcohol on the Low-Melting Chloride.—Ten grams of the low-melting chloride were dissolved in 30 or 40 cc. of cold methyl alcohol, and the solution allowed to stand 2 hours. At the end of that time the alcohol was evaporated by warming the solution and drawing air through it. When the proper concentration had been reached, very small, diamond-shaped crystals separated from the solution. The evaporation was continued until no more crystals deposited, when they were filtered off and washed with water to remove the alcohol and hydrochloric acid which is formed in the reaction. The substance agreed in most of its properties with that prepared by Bird. It is soluble in alcohol and ether, but insoluble in water. Cold alkali, whether concentrated or dilute, has no effect upon the compound, but on boiling it dissolves and chlorine is removed. The melting-point, 63°–64° (uncorr.), is rather higher than that given by Bird, but it is probable that his material was somewhat impure, since his figures differ considerably from the calculated values.

Analysis[1]:

0.1062 gram substance gave 0.1592 gram CO_2 and 0.0276 gram H_2O.

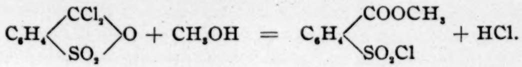
0.2354 gram substance gave 0.2401 gram $BaSO_4$ (Carius).

To determine the chlorine the substance was saponified by heating with pure sodium hydroxide and titrated to neutrality with nitric acid. The chlorine was then determined with a 0.1 N solution of silver nitrate. Sodium chromate was used as the indicator:

0.1835 gram substance required 7.8 cc. 0.1 N $AgNO_3$.

	Calculated for $C_6H_4\begin{cases}COOCH_3\\SO_2Cl\end{cases}$.	Found.
C	40.90	40.88
H	3.01	2.92
Cl	15.11	15.06
S	13.66	14.00

The reaction is to be expressed as follows:



The action of boiling ethyl and methyl alcohols has been fully investigated by former workers.[2] The reaction with methyl alcohol was repeated and the product was found to be the ester acid. No trace of the oil containing chlorine, as described by Bird, was obtained. The analogous reactions with ethyl alcohol have already been given.

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[1] The method employed for the determination of carbon and hydrogen was that described by Morse and Taylor: THIS JOURNAL, **33**, 591. See also L. S. Taylor, Dissertation, J. H. U., 1905.

[2] Remsen and Dohme: THIS JOURNAL, **11**, 341. Remsen and Karslake: *Ibid.*, **18**, 825.

Action of Methyl Alcohol on the High-Melting Chloride.—On the high-melting chloride the alcohols, in general, react with less ease than upon the low-melting chloride. Upon boiling, however, the ester acids are also produced.

By boiling either chloride with 95 per cent ethyl alcohol for some hours, Bird obtained an acid of which the barium salt contained from 28 to 29.5 per cent of barium. Humphreys[1] had already obtained the same acid by boiling the orthosulphone chloride of phenyl benzoate for 12 hours, in absolute alcohol.

In the course of the present investigation the reaction described by Bird was repeated, with the hope of obtaining some light on the composition of this acid. Five grams of the high-melting chloride were boiled for 13 hours with absolute ethyl alcohol. The formation of ethyl chloride was continuous. After the reaction was over the alcohol was distilled off, and the remaining hydrochloric acid was expelled by heating on the water-bath. The product was dissolved in water, filtered from the small insoluble residue and boiled with barium carbonate until no more was dissolved. After crystallization the salt was dried and analyzed for barium; 0.1800 gram of substance gave 0.868 gram $BaSO_4$. Found: Ba, 28.37 per cent. This was evidently the same acid that had been obtained by Humphreys and Bird. Since no formula could be assigned to the substance from the analysis of its barium salt, an effort was made to learn its structure in another way. The experiment was repeated with an equal quantity of the chloride and the barium salt prepared as before. This was converted into the sodium salt and, after evaporating to dryness, the salt was treated with phosphorus pentachloride. Reaction took place immediately. After heating some time to expel the oxychloride, water and ice were added and the material was ground until all traces of the oxychloride had been removed.

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[1] Dissertation, J. H. U., 1900.

After washing several times with water, strong ammonia was added and the mixture was warmed on the water-bath. The solutions became sweet and, with hydrochloric acid, gave a heavy precipitate of saccharin. This experiment pointed to the presence of orthosulphobenzoic acid. The following considerations lead to the same conclusion: The action of boiling alcohol on the chlorides is known to produce the ester acid. Further action of the alcohol yielded the unidentified acid. The action of alcohol on the phenyl ester chloride must first convert it into the ester acid. Upon further boiling, the unidentified acid was also formed. These facts show that a change in the carboxyl group must have taken place. The action of phosphorus pentachloride, already referred to, showed the acid to be dibasic. The ethyl esters of carboxyl acids are not saponified by absolute alcohol, however, and a special reason must be sought in this case. It has been stated that ethyl chloride was formed constantly and for every molecule of ethyl chloride 1 molecule of water must have resulted. The tendency of the water should be to saponify the ester and there would result an equilibrium between orthosulphobenzoic acid and the ester acid. In the experiments performed by Bird he obtained the acid after boiling with 95 per cent alcohol for 3 hours, while in the experiments last described it was necessary to heat with absolute alcohol for 13 hours. Providing that all of the hydrochloric acid formed in this reaction reacted with the alcohol, then, for every molecule of chloride used, enough water would be formed to saponify 2 molecules of the ester acid. The presence of the alcohol would cause an equilibrium to exist between the ester acid and orthosulphobenzoic acid. It appears, therefore, that the salt containing about 28 per cent barium is probably a mixture of a salt of orthosulphobenzoic acid and a salt of the ester acid.

III. Action of Sodium Ethylate on the Chlorides.

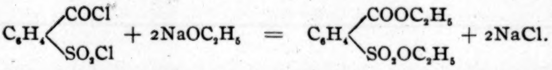
High-Melting Chloride.—Five grams of the high-melting chloride were dissolved in dry ether and an alcoholic solution of sodium ethylate was gradually added until the reaction ceased. The experiment is best carried out in a bottle, which may be corked and well shaken from time to time, because the precipitated sodium chloride is voluminous and interferes with the reaction. In no case were less than 2 molecules of ethylate required. The action never stopped half way, and the addition of an excess of ethylate was often found necessary in order that the reaction might be complete. After the action was over, the resulting mixture was poured into a separating-funnel containing acidulated water. The contents were thoroughly shaken until the sodium chloride and excess of ethylate were dissolved, when the aqueous layer was run off. The ethereal layer was washed several times with water, then removed and dried over calcium chloride for 12 hours. After filtration and evaporation of the ether an oil remained which was soluble in alcohol and ether, but insoluble in water. It was neutral to litmus. Various methods for its purification were tried, but none was successful until distillation under reduced pressure was employed. Analysis:

0.1540 gram substance gave 0.2899 gram CO_2 and 0.0738 gram H_2O.

0.3493 gram substance gave 0.3243 gram $BaSO_4$.

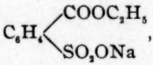
	Calculated for $C_6H_4\langle{}^{COOC_2H_5}_{SO_2OC_2H_5}$.	Found.
C	51.12	51.33
H	5.47	5.37
S	12.41	12.74

These values point conclusively to the formula of the diethyl ester. It boils at 212°–213° (21 mm.). At this pressure the ester distils with very little decomposition, It should be allowed to stand after distillation, for some hours, as a few crystals of sulphobenzoic anhydride usually separate. They can be removed by filtration. At a greater pressure, however, the ester distils with much decomposition. Among the products formed are sulphobenzoic anhydride and ethyl benzoate. The former was identified by its melting point (129°.5), and by its conversion into sulphonefluorescein when fused with resorcinol. The ethyl benzoate was detected by its odor. The reaction is expressed by the equation:



$$C_6H_4\left\langle\begin{matrix}COCl\\SO_2Cl\end{matrix}\right. + 2NaOC_2H_5 = C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2OC_2H_5\end{matrix}\right. + 2NaCl.$$

The yield of ester by this method was always small. The fact, established by Bird, that when the mass is allowed to stand a salt of the formula,



$$C_6H_4\left\langle\begin{matrix}COOC_2H_5\\SO_2ONa\end{matrix}\right.,$$

is formed, suggested the explanation of the small yield. The alcohol used as the solvent for the ethylate would tend to saponify the ester, and the acid thus formed would be converted into its sodium salt by the action of the ethylate. To test this point the experiment was repeated as above, except that no alcohol was used, the ethylate being added in the dry state to the ethereal solution of the chloride. The yield of ester was almost theoretical. No sulphone chloride was obtained in the experiments.

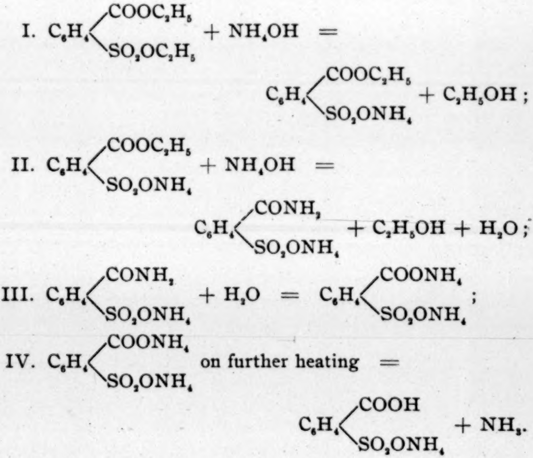
Upon boiling the impure ester with ammonia a sweet compound was usually produced, and sometimes a precipitate of saccharin appeared upon acidification. No such reaction takes place with the pure ester, however. Furthermore, the impure ester always gives a test for chlorine, while the pure substance is entirely free from it. These facts show that a small quantity of unchanged chloride is usually present in the impure ester. They also tend to explain certain observations made by Bird, which have already been referred to.

It is a fact that the action of ammonia upon the ester produces a substance which has an acid reaction. The ester is boiled, with frequent additions of concentrated ammonia, until it dissolves. This operation requires half an hour or longer. The solution is then evaporated to the proper concentration and allowed to cool. If the ammonia gas has all been expelled from the solution, the acid ammonium salt of orthosulphobenzoic acid separates. A determination of the nitrogen in the salt showed this to be the case.

0.1097 gram substance gave 0.006858 gram N (absolute).

	Calculated for $\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COOH}\\\mathrm{SO_2ONH_4}\end{matrix}\right.$.	Found.
N	6.40	6.25

In order to obtain confirmatory evidence, if possible, a quantity of the acid ammonium salt of orthosulphobenzoic acid, which had been made by the hydrolysis of saccharin, was dissolved in an excess of strong ammonia and the solution evaporated. After the odor of ammonia had disappeared the solution was found to have become acid and crystals of the acid ammonium salt were obtained upon further evaporation. Ammonium sulphobenzoate was found to behave in the same way. The reactions must be expressed as follows:



$$\text{I. } \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{SO_2OC_2H_5}\end{matrix}\right. + \mathrm{NH_4OH} = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{SO_2ONH_4}\end{matrix}\right. + \mathrm{C_2H_5OH};$$

$$\text{II. } \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COOC_2H_5}\\\mathrm{SO_2ONH_4}\end{matrix}\right. + \mathrm{NH_4OH} = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{CONH_2}\\\mathrm{SO_2ONH_4}\end{matrix}\right. + \mathrm{C_2H_5OH} + \mathrm{H_2O};$$

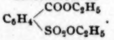
$$\text{III. } \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{CONH_2}\\\mathrm{SO_2ONH_4}\end{matrix}\right. + \mathrm{H_2O} = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COONH_4}\\\mathrm{SO_2ONH_4}\end{matrix}\right.;$$

$$\text{IV. } \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COONH_4}\\\mathrm{SO_2ONH_4}\end{matrix}\right. \text{ on further heating } = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{COOH}\\\mathrm{SO_2ONH_4}\end{matrix}\right. + \mathrm{NH_3}.$$

With saponifying agents, the first point of attack is the sulphonic acid group. With aqueous alkali the ester is only slowly changed owing to its insolubility in water, but when alcoholic alkali is employed the reaction proceeds with ease. The final product of the action of alkalis is the neutral salt of orthosulphobenzoic acid. Aqueous ammonia acts more easily than aqueous alkali.

Low-Melting Chloride.—The action of sodium ethylate on the low-melting chloride also results in the formation of the diethyl ester. The ester agrees in all its properties with the one prepared from the high-melting chloride. Analysis:

0.1537 gram substance gave 0.2863 gram CO_2 and 0.0794 gram H_2O.

	Calculated for  $C_6H_4\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases}$.	Found.
C	51.12	51.46
H	5.47	5.86

The reaction was tried under various conditions, an alcoholic solution of sodium ethylate was added to the dry chloride; the chloride, in ether, was treated with an alcoholic solution of the ethylate, and, finally, dry ethylate was added to an ethereal solution of the chloride. The last was found to be the most satisfactory method.

The neutral oils soluble in water, which are described by Bird, have not been obtained.

On grinding together dry sodium ethylate and dry, low-melting chloride, Bird obtained a product that he was not able to identify. The reaction is explosive and difficult to control. Furthermore, more or less decomposition takes place. On repeating the reaction the substances were mixed, in very small portions, in a large test-tube and stirred with a glass rod. After the reaction, water and ether were added and the tube was shaken. The ether was found to contain a little oil in a very impure state and in quantity insufficient for distillation. It was neutral and insoluble in water, however, and there seems to be no reason for doubting that it was the diethyl ether.

IV. Action of Benzene and Aluminium Chloride.

The action of benzene on the chlorides, in the presence of aluminium chloride, was first studied by Remsen and Saunders.[1]

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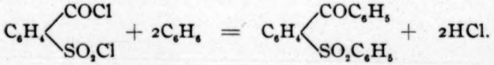
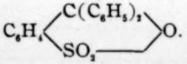
[1] THIS JOURNAL, 17, 347.

They showed that the high-melting chloride reacts to form, as the final product, orthobenzoyldiphenylsulphone, as follows:



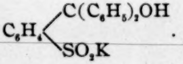
$$C_6H_4\left<\begin{matrix}COCl\\ SO_2Cl\end{matrix}\right. + 2C_6H_6 = C_6H_4\left<\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix}\right. + 2HCl.$$

This substance melts at 183°–184°. In studying the reaction with a mixture of the two chlorides, by far the largest portion of the product was the same substance. They obtained simultaneously, however, another compound, melting at 162°–163°. Analysis showed it to be of the same empirical formula as the first one, but its conduct, when fused with potassium hydroxide, led them to assign to it the formula of the lactone,



$$C_6H_4\left<\begin{matrix}C(C_6H_5)_2\\ SO_2\end{matrix}\right>O.$$

In their article upon the chlorides of orthosulphobenzoic acid, List and Stein[1] also describe the substance. They obtained it by the action of benzene and aluminium chloride upon the mixed chlorides. The reaction was allowed to proceed at the ordinary temperature for some days, after which the mixture was warmed for a time. The substance dissolved in boiling, alcoholic potassium hydroxide with the formation of a potassium salt of the formula



$$C_6H_4\left<\begin{matrix}C(C_6H_5)_2OH\\ SO_3K\end{matrix}\right. .$$

Upon treatment with acids the lactone was recovered.

Since it has been possible to isolate the low-melting chloride in a pure condition, many attempts have been made to prepare this substance. None of them has been successful, the sole product of the reaction being always the symmetrical compound, orthobenzoyldiphenylsulphone, identical with that derived from the high-melting chloride.

The writer made several attempts to obtain the lactone by the action of benzene and aluminium chloride upon the low-melting chloride, but always without success. The reaction was allowed to take place at the room temperature, during a period of 3 or 4 days, and also at the temperature of a boiling water-bath, when it is complete in a short time. Finally, a mixture of 60 per cent of the low-melting chloride and 40 per cent of the high-melting chloride was dissolved in pure, dry benzene, and aluminium chloride was added from time to time. The reaction was allowed to proceed at the room temperature. The resulting product was found to be symmetrical however, no trace of the lactone being formed. The proportion of the two chlorides taken is about that in which they occur in the mixture which is obtained by the action of phosphorus pentachloride on the acid potassium salt. It was with this mixture that List and Stein obtained their results.

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[1] Ber. d. chem. Ges., 31, 1648.

From the experiments of former workers, as well as from those last recorded, it would seem doubtful if the product first described by Remsen and Saunders, and later by List and Stein, was in reality the lactone as supposed. A substance has been obtained by another method, however, and will be described presently, which analysis shows to be the lactone and which, moreover, agrees with the description of the lactone made as above. Such being the case, the conclusion must be that the action of benzene and aluminium chloride has, in two instances at least, given the lactone. From the failure of other workers to obtain it, it is evident that peculiar conditions must be necessary to its formation.

V. Experiments with Thionyl Chloride.

Since the methods which are employed for the preparation of the chlorides, especially in the case of the low-melting one, fail to give satisfactory yields, it seemed desirable to try the action of thionyl chloride on both the acid and neutral salts, in the hope that this reagent might give better results than the pentachloride or oxychloride of phosphorus.

Ten grams of the dried and finely pulverized neutral potassium salt of orthosulphobenzoic acid were placed in a small balloon flask, and an equal weight (2.5 mol.) of thionyl chloride was added. The flask was fitted to a return condenser, which was provided at its upper end with a Peligot tube containing a strong solution of sodium hydroxide, to absorb the sulphur dioxide which was given off. The reaction started without the application of heat, but did not become vigorous. At the temperature of the boiling water-bath, however, it progressed rapidly. The heating was continued until no more sulphur dioxide was liberated, about 45 minutes being required. During the progress of the reaction the mass became more and more viscous, until at the end the appearance had become like that of thick starch paste. The condenser was then reversed and the excess of thionyl chloride was distilled off. This process was much facilitated by slightly diminishing the pressure. After the removal of the excess of thionyl chloride, the mass became crystalline. It was removed from the flask and ground in a mortar with water containing ice, and then poured into a separating funnel and shaken with ice-water and ether. A portion of the material did not immediately go into solution but dissolved gradually, as the shaking was continued. After removing the ethereal layer it was examined with the expectation of finding one or both of the chlorides of orthosulphobenzoic acid. All that was obtained, however, was a small quantity of the anhydride of orthosulphobenzoic acid which had escaped hydrolysis in the treatment with water. A portion of this material, which did not dissolve readily, was filtered off and examined. It was found to contain potassium and chlorine, and to show an acid reaction with litmus. On boiling with water it was dissolved and hydrochloric acid was formed. A small quantity was dried on a porous plate and placed in a desiccator over sulphuric acid. It was hoped in this way to obtain a specimen for analysis in fairly pure condition, but upon opening the desiccator, some hours later, fumes of hydrochloric acid escaped, showing that the substance had been hydrolyzed. No further effort was made to obtain the pure compound, but its composition was shown by another method.

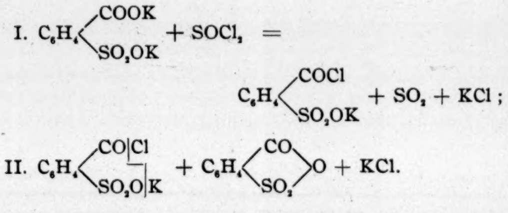
The reaction between the neutral salt and thionyl chloride was repeated in the manner above described, but after distilling off the excess of the latter, absolute alcohol was added and the mixture boiled. At the end of an hour the alcohol was filtered off. Upon cooling, crystals separated in the form of thin leaves, these were removed and analyzed for potassium :

0.1050 gram substance gave 0.334 gram K_2SO_4.

	Calculated for $C_6H_4\Big\langle\begin{matrix}COOC_2H_5\\SO_2OK\end{matrix}$.	Found.
K	14.59	14.28

The yield of these crystals was only about 0.5 gram, showing that the reaction had, for the most part, progressed beyond the first stage. That even a small quantity of this salt was obtained, however, points conclusively to the presence of a compound of the formula $C_6H_4\Big\langle\begin{matrix}COCl\\SO_2OK\end{matrix}$. That the structure of this monochlorinated derivative of the neutral potassium salt is that which has been assigned to it, rather than that of the isomeric sulphone chloride, $C_6H_4\Big\langle\begin{matrix}COOK\\SO_2Cl\end{matrix}$, is evident from the fact that it is converted into an ester upon boiling with alcohol, a reaction which does not occur with the sulphone chlorides.

The formation of the anhydride, then, takes place in two stages, the first product being a monochlorinated derivative which passes into the anhydride by loss of potassium chloride :



$$\text{I. } C_6H_4\Big\langle\begin{matrix}COOK\\SO_2OK\end{matrix} + SOCl_2 = C_6H_4\Big\langle\begin{matrix}COCl\\SO_2OK\end{matrix} + SO_2 + KCl;$$

$$\text{II. } C_6H_4\Big\langle\begin{matrix}CO|Cl\\SO_2O|K\end{matrix} = C_6H_4\Big\langle\begin{matrix}CO\\SO_2\end{matrix}\Big\rangle O + KCl.$$

The next experiment was performed with the intention of determining whether or not the anhydride could profitably be prepared by this method. Thirty-four grams of the neutral potassium salt were treated with a large excess (5 or 6 mols.) of thionyl chloride and heated on the water-bath until no more sulphur dioxide escaped. About one hour was required. The excess of thionyl chloride was then distilled off and the residue in the flask was extracted with dry benzene. Only 7 grams (31 per cent) of the anhydride were obtained, however. It is probable that if the heating had been allowed to proceed longer, the yield would have been larger, but the experiment was not repeated with the neutral salt, since the acid salt was found to give much more satisfactory results.

The final experiment with the neutral salt was an attempt to prepare a chloride of orthosulphobenzoic acid. Twenty grams of thionyl chloride were poured into a Carius tube, an equal weight of the neutral salt added and a thorough mixture made. After heating at 125°, for 13 hours, the tube was opened and found to contain anhydride, but no chloride was present. In order to isolate the chloride, if formed, the reaction mixture was shaken with water, ice and ether. Since the greater part of the anhydride was hydrolyzed by this process, the quantity formed was not determined.

Experiments with the Acid Salt.—Both the neutral and acid potassium salts of orthosulphobenzoic acid are attacked with about the same ease by thionyl chloride. With the acid salt the reaction takes place with the formation of hydrochloric acid, showing that the point of attack is the carboxyl. With the acid salt, as with the neutral, no chloride was obtained either under the ordinary pressure or in a sealed tube. As a method of preparing the anhydride, however, the action of thionyl chloride was found to be very satisfactory. Two experiments were conducted; in the first, 10 grams of the acid salt were heated on the water-bath with a large excess of thionyl chloride. The reaction was complete in 45 minutes. After distilling off the excess of thionyl chloride, the residue was extracted with dry benzene. Four grams of the anhydride were obtained, which corresponds to a yield of 52 per cent.

The second experiment was conducted with somewhat larger quantities. Twenty-seven grams of the acid salt were heated on the water-bath with 56 grams of thionyl chloride. The volatile reaction products ceased to escape in about an hour, but the mixture was heated for 1.5 hours longer, and was then treated in the usual way. Sixteen and five-tenths grams (80 per cent) of the anhydride were obtained.

In order to get the best results, it has been found advisable to use a large excess of thionyl chloride, by so doing the mixture remains in a semi-liquid state, and better contact is secured. It is also advisable to heat for an hour or two after the volatile reaction products have ceased to escape. The thionyl chloride recovered is quite pure and may be used again.

The results of these experiments indicate that the normal reaction of chlorinating agents on both the acid and neutral salts is the formation of a monochlorinated derivative containing the chlorine in combination with the carbonyl. This passes into the anhydride by the loss of potassium chloride. The formation of the two dichlorides of orthosulphobenzoic acid remains to be explained. In the preparation of the high-melting chloride, about 60 per cent of the low-melting chloride is also produced. When the neutral salt is treated in the same manner a mixture is also obtained. In this case the chlorinating agent is phosphorus pentachloride. On the other hand, in the preparation of the low-melting chloride by the action of phosphorus oxychloride on the neutral salt, practically none of the high-melting chloride is formed. The formation of the high-melting chloride, then, is favored by the action of a powerful chlorinating agent.

List and Stein[1] have shown that the action of phosphorus pentachloride on the anhydride, at high temperatures, gives rise to the formation of both chlorides. For the sake of comparison, the action of the oxychloride upon the anhydride was tried. Twelve grams of the anhydride were heated for 14 hours with phosphorus oxychloride, at 125°. At the end of that time the mixture was examined and it was found that, while the reaction was by no means complete, about 2 grams of the low-melting chloride had been formed. It was identified by its melting point. In order to test for the presence of high-melting chloride, ammonia was added but no sweet taste was produced. The action of phosphorus pentachloride probably takes place as follows: The anhydride is first formed and it is attacked in two ways by the pentachloride, with the formation of two isomeric substances. The action of the oxychloride can take place in only one way, however, since only one product is formed. If the action of the oxychloride were not considered, one might assume that with the pentachloride the reaction all goes in one direction, and that a rearrangement takes place. The fact that neither chloride can be changed into the other by heat, also argues against the latter supposition. The pentachloride, then, must have the power to chlorinate both the carbonyl group of the anhydride and also to replace the anhydride oxygen atom. It would be expected that the latter reaction would take place with the greater difficulty and, as already stated, the yield of high-melting chloride, when prepared from the acid salt, is only 40 per cent of the total. The oxychloride can only attack the carbonyl group, while, ashas been shown, thionyl chloride does not react with the anhydride:

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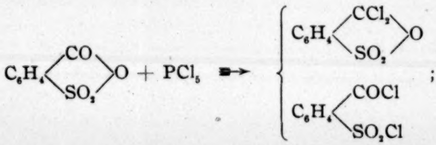
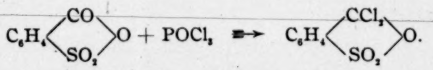
[1] Ber. d chem. Ges., 31, 1659.





VI. Experiments with Magnesiumphenyl Bromide.

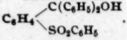
Action on the High-Melting Chloride.—With the high-melting chloride magnesiumphenyl bromide reacts only at the boiling point of ether, while with the low-melting chloride the reaction is so violent that the solutions must be cooled with ice and mixed very slowly. The resulting products are very difficult to purify. In the case of the high-melting chloride the product has been fully identified, while with the low-melting chloride satisfactory results have not been obtained.

Ten grams of the high-melting chloride were dissolved in dry ether, and to the solution an ethereal solution of 3.5 molecules of magnesiumphenyl bromide was added. The mixture was boiled for an hour or two until the oily substance which settled to the bottom of the flask did not increase in quantity. At this point the ether above the oil had become clear. The ether was then poured off and the residue in the flask was shaken with water and dilute hydrochloric acid. After the decomposition had been effected, the resulting oil was allowed to settle and the water and acid were poured off. It was washed with several changes of water. Steam was then conducted into the flask to remove any brombenzene which might have been present. After many unsuccessful attempts to purify this oil, the following method was found satisfactory: The oil was allowed to stand under water for a week or more. At the end of this time it had usually solidified, for the most part. It was then heated to boiling with methyl alcohol and the alcohol poured off while still hot. This treatment removed the unsolidified portion. The solid remaining was then crystallized from ethyl alcohol. The oil is easily soluble in alcohol and ether. After solidification, however, it is soluble in these liquids with much greater difficulty.

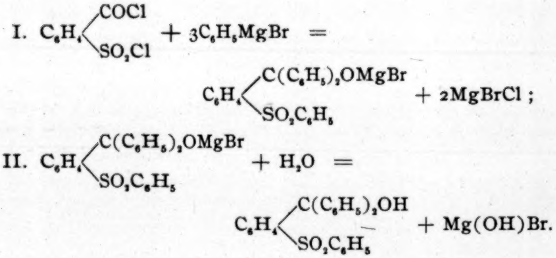
The product which had been crystallized from alcohol melted at 183°–184°. It is not affected by alcoholic potassium hydroxide. With concentrated nitric and sulphuric acids a dark red color is produced, an indication of the carbinol condition. Analysis:

0.1284 gram substance gave 0.3509 gram CO_2 and 0.0603 gram H_2O.

0.2146 gram substance gave 0.1268 gram $BaSO_4$ (Carius).

	Calculated for  $C_6H_4\begin{cases}C(C_6H_5)_2OH\\SO_2C_6H_5\end{cases}$.	Found.
C	74.95	74.52
H	5.04	5.26
S	8.00	8.11

The reaction must be represented as follows:



$$\text{I. } C_6H_4<\begin{matrix}COCl\\ SO_2Cl\end{matrix} + 3C_6H_5MgBr = C_6H_4<\begin{matrix}C(C_6H_5)_2OMgBr\\ SO_2C_6H_5\end{matrix} + 2MgBrCl;$$

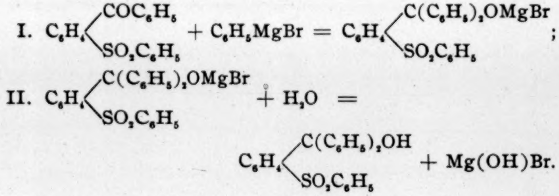
$$\text{II. } C_6H_4<\begin{matrix}C(C_6H_5)_2OMgBr\\ SO_2C_6H_5\end{matrix} + H_2O = C_6H_4<\begin{matrix}C(C_6H_5)_2OH\\ SO_2C_6H_5\end{matrix} + Mg(OH)Br.$$

The structure of this substance was established by treating orthobenzoyldiphenylsulphone with magnesiumphenyl bromide. The product thus obtained melted at the same temperature, and the melting point of a mixture of the two preparations remained unchanged. Analysis:

0.1378 gram substance gave 0.3783 gram CO_2 and 0.0661 gram H_2O.

	Calculated for $C_6H_4<\begin{matrix}C(C_6H_5)_2OH\\ SO_2C_6H_5\end{matrix}$.	Found.
C	74.95	74.86
H	5.04	5.37

The reaction is represented by the equations:



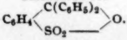
$$\text{I. } C_6H_4<\begin{matrix}COC_6H_5\\ SO_2C_6H_5\end{matrix} + C_6H_5MgBr = C_6H_4<\begin{matrix}C(C_6H_5)_2OMgBr\\ SO_2C_6H_5\end{matrix};$$

$$\text{II. } C_6H_4<\begin{matrix}C(C_6H_5)_2OMgBr\\ SO_2C_6H_5\end{matrix} + H_2O = C_6H_4<\begin{matrix}C(C_6H_5)_2OH\\ SO_2C_6H_5\end{matrix} + Mg(OH)Br.$$

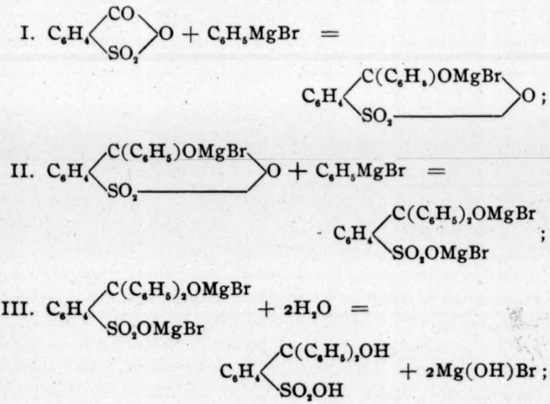
Action on Sulphobenzoic Anhydride.—The reaction of magnesiumphenyl bromide on sulphobenzoic anhydride was tried, in the hope of obtaining a diphenylated derivative. This product was obtained and has been referred to under the reaction of benzene and aluminium chloride. The action is vigorous, and the solutions should be cooled with ice. After standing some time, water and sulphuric acid were added and the contents of the flask were well shaken with ether. Upon examination of the ethereal layer a product was obtained which, when crystallized from alcohol, melted sharply at 163° (uncorr.). It dissolved in alcoholic potassium hydroxide, on boiling, with the formation of a salt soluble in water. Upon acidification the original substance was precipitated. Neither water nor aqueous potassium hydroxide would dissolve the substance even when boiled. Analysis:

0.1070 gram substance gave 0.2772 gram CO_2 and 0.0447 gram H_2O.

0.2056 gram substance gave 0.1564 gram $BaSO_4$ (Carius).

	Calculated for  $C_6H_4{<}\begin{matrix}C(C_6H_5)_2\\SO_2\end{matrix}{>}O.$	Found.
C	70.76	70.64
H	4.38	4.68
S	9.95	10.40

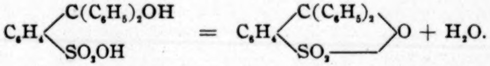
The reaction may be expressed as follows:



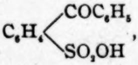
$$\text{I.}\quad C_6H_4{<}\begin{matrix}CO\\SO_2\end{matrix}{>}O + C_6H_5MgBr \;=\; C_6H_4{<}\begin{matrix}C(C_6H_5)OMgBr\\SO_2\end{matrix}{>}O\,;$$

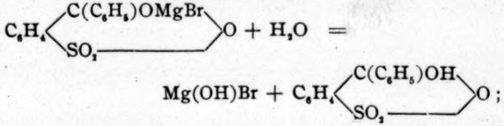
$$\text{II.}\quad C_6H_4{<}\begin{matrix}C(C_6H_5)OMgBr\\SO_2\end{matrix}{>}O + C_6H_5MgBr \;=\; C_6H_4{<}\begin{matrix}C(C_6H_5)_2OMgBr\\SO_2OMgBr\end{matrix}\,;$$

$$\text{III.}\quad C_6H_4{<}\begin{matrix}C(C_6H_5)_2OMgBr\\SO_2OMgBr\end{matrix} + 2H_2O \;=\; C_6H_4{<}\begin{matrix}C(C_6H_5)_2OH\\SO_2OH\end{matrix} + 2Mg(OH)Br\,;$$

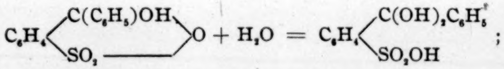
IV. 

$$C_6H_4\left<\begin{matrix}C(C_6H_5)_2OH\\ SO_2OH\end{matrix}\right. = C_6H_4\left<\begin{matrix}C(C_6H_5)_2\\ SO_2\end{matrix}\right>O + H_2O.$$

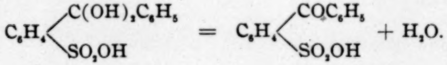
The substance just described is formed to the extent of only about 10 per cent. It is probable that the reaction, in the main, stops at stage I. The product would then be hydrolyzed to form the acid,  $C_6H_4\left<\begin{matrix}COC_6H_5\\ SO_2OH\end{matrix}\right.$, as follows:

I. 

$$C_6H_4\left<\begin{matrix}C(C_6H_5)OMgBr\\ SO_2\end{matrix}\right>O + H_2O = Mg(OH)Br + C_6H_4\left<\begin{matrix}C(C_6H_5)OH\\ SO_2\end{matrix}\right>O;$$

II. 

$$C_6H_4\left<\begin{matrix}C(C_6H_5)OH\\ SO_2\end{matrix}\right>O + H_2O = C_6H_4\left<\begin{matrix}C(OH)_2C_6H_5\\ SO_2OH\end{matrix}\right.;$$

III. 

$$C_6H_4\left<\begin{matrix}C(OH)_2C_6H_5\\ SO_2OH\end{matrix}\right. = C_6H_4\left<\begin{matrix}COC_6H_5\\ SO_2OH\end{matrix}\right. + H_2O.$$

This compound is not of any special interest and no attempt was made to separate it. Since the substance is soluble in water, it did not appear in the ethereal extract of the products.

JOHNS HOPKINS UNIVERSITY.

NOTE ON "THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES."

BY ROGER CLARK WELLS.

In the article by me in the February number of this JOURNAL, there was, I regret to state, an incorrect conclusion. In trying to estimate the magnitude of possible error upon the determination of the atomic weight of sodium due to time effects in nephelometry, I based my reasoning upon the behavior of intense opalescences, whereas, really, only weak opalescences were concerned. Professor Richards, to whom I had, unfortunately, not presented the paper for preliminary reading, immediately called my attention to this and I am very glad to correct it. It results, therefore, that the correction, if any, must be even less than 0.001 of a unit in the atomic weight of sodium and, hence, quite negligible.

Lest some may attach too much significance to the times of maximum opalescences, I wish to emphasize the fact that the opalescences, especially weak ones, are changing very slowly just before and after their maxima, so that the exact time to a minute means little. Moreover, the variation is occasionally large. The anomalous results illustrating this, referred to in the foot-note on p. 111, were probably due to an insufficient excess of precipitant. Previous work had shown that a long time was often necessary for the opalescences to become relatively stable. My experiments were made to discover the means by which to obtain the maximum opalescence as speedily as possible, and showed that, under the conditions mentioned, on the average, intense opalescences become relatively stable in from 1 to 20 minutes, medium opalescences in from 10 to 40 minutes and weak opalescences in 30 minutes or over.

The maximum was chosen as the best measure of the opalescence, and it could always be found by comparing the opalescence at any time with an unchangeable ground glass. In consequence of the time effects above noted, such a method is more necessary for intense opalescences, which change quickly, than for weak ones which change very slowly. In the case of weak opalescences, the older procedure of waiting a long time before reading, two tubes would yield almost precisely the same result as reading each at its maximum.

In brief, then, as far as time effects in nephelometry are concerned, the time factor must be carefully regulated for intense opalescences, but it ceases to be a major variable with weak ones.

Contribution from the Chemical Laboratory of Harvard College.

NOTE CONCERNING THE USE OF THE NEPHELOMETER.

By Theodore William Richards.

A recent article by Dr. R. C. Wells upon "The Estimation of Opalescent Silver Chloride Precipitates" with the help of the nephelometer[1] seems to call for a few additional remarks. The following note is written in order to supplement his suggestions, and to point out clearly the range of applicability of nephelometric methods.

Dr. Wells' conclusions are based upon a series of comparisons in which the cloudiness of a ground glass plate was used as the standard of comparison with the cloudiness produced by opalescent precipitates. This is a good idea, but it is evident that the intensity of light reflected to the eye-piece from this plate will vary with the inclination of the plate to the source of light and, therefore, that great care must be taken to have this inclination always definite. Undoubtedly, this was taken into account, but the necessity of this precaution was not sufficiently emphasized.

Another cause of uncertainty which, although mentioned as a possible source of error, and also heeded to some extent, may not have been quite sufficiently guarded against in the experimental work, is variation in temperature. Silver chloride is much more soluble in hot than in cold water, and the form of aggregation of the precipitate varies greatly with the temperature. Both these facts cannot but affect the rate of formation of the opalescent precipitate; hence, any work aiming at definite comparison with a fixed standard should be conducted in thermostatted tubes.

Qualitatively, it has been known for many years that the rate of decay of the opalescence, as well as the rate of precipitation, varies greatly with the "concentration" of the precipitate, in other words, with the weight of precipitate suspended in a given volume of liquid. An intense opalescence settles out much more quickly than a faint one. Dr. Wells has quantitatively estimated this difference of behavior. A saturated solution of silver chloride, such as is usually studied by means of the nephelometer, ordinarily contains not much over 1.5 milligrams per liter, or is only about 0.00001 N; but two-thirds of the figures given by Dr. Wells refer to solutions as strong as 0.00004 N, nearly four times as concentrated. While it is a matter of great interest to study, as Dr. Wells has done, the rapid rate of deposition of these more concentrated opalescences, they should probably not be made the basis of exact quantitative analytical work, because of their rapid rate of change. For quantitative estimation of the substance in such mixtures, it is better not to use the nephelometer, but to collect the precipitate after it has been wholly deposited. The nephelometer should be employed for exact work only when the precipitate is so finely divided that it will not in any reasonable time, for example 2 or 3 days, deposit itself and thus place itself within the range of ordinary quantitative determination.

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[1] This Journal, 35, 99 (1906).

It should be strongly emphasized that the "anomalous results" mentioned by Dr. Wells had been duly considered in previous work, and were distinctly pointed out, but the bulk of the previous papers was concerned with indicating the way in which the difficulties can be overcome; therefore but few figures were given.

While the ground glass plate employed by Dr. Wells, when properly and steadily illuminated, undoubtedly affords an excellent means of studying the rate of change in a given mixture, I cannot believe that it provides the best standard of reference for analytical purposes, because it is unaffected by the many variables which affect the mixture to be estimated. In my opinion, if even moderately accurate analytical results are to be had with the nephelometer, the one essential point to be heeded is this: ***the unknown solutions to be estimated must be treated in exactly the same way as the known standard solutions, which serve as the basis of comparison.*** If this precaution is adhered to, the changes of temperature, the presence of electrolytes, the concentration of the solutions and all the other variables, affecting each precipitate in like manner, are eliminated from the comparison. This method, indeed, is a fundamental principle in all precise volumetric analysis.

That this precaution was realized in the previous discussion of the instrument may be shown by the following quotation :

"Care must be taken to have both standard solution and unknown solution subjected to precisely the same conditions, for varying conditions of precipitation may lead to differences in the appearance of the precipitate far greater than the possible optical error of the apparatus. Herein lies the chief caution to be noted in its use."

"The contents of this paper may be summarized as follows : . . . . . The chief possibility of error lies in the state of the precipitated material. In order to exclude variation here, the solution to be estimated and the standard solution for comparison should be precipitated in exactly the same way."[1]

On the same page with these statements is to be found a series of results showing, positively, that when this advice is heeded, and when sufficient time is allowed for the opalescence to develop, the instrument gives reasonably accurate results, and similar evidence is given in another place.

In the course of the work upon the atomic weight of sodium, a singular anomaly was observed, namely, the fact that the opalescence of silver chloride forms more quickly when a solution of this salt is treated with a large excess of silver nitrate than it does when an equivalent solution of sodium chloride is treated in the same way. This irregularity leads to an uncertainty as to whether the *weights* of precipitate corresponding to a given maximum intensity of opalescence are equal in the two cases—an uncertainty clearly pointed out in the place mentioned. The question of weight is not discussed in Dr. Wells' paper, but is now being exhaustively studied at Harvard. The uncertainty arose only because of a slight infringement of the rule italicized above. When the two mixtures are subjected to the same conditions—for example, when both are redissolved in ammonia and reprecipitated, the uncertainty disappears. This practice is being adopted in a research on the atomic weight of potassium, now being pursued at Harvard by Dr. A. Stähler, of Berlin, and the author.

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[1] Richards and Wells : This Journal, 31, 242 (1904). It should be noted that both these sentences were written by the author, who takes all the responsibility attached to them.

In brief, the object of this note may be summarized as follows: It is pointed out that, while the recent paper of Dr. R. C. Wells on the nephelometer affords interesting data concerning the rate of precipitation of opalescent precipitates, particularly in cases verging upon prompt deposition, it does not emphasize the chief precaution which, in the author's opinion, should be adopted if the nephelometer is to be used in quantitative analytical work.

Contributions from the Chemical Laboratory of Harvard College.

ISOHEXANE AND A NEW DODECANE.

BY LATHAM CLARKE AND R. NORRIS SHREVE.

As the preparation of isohexane, according to Wurtz,[1] from isobutyl iodide, ethyl iodide and sodium, is unsatisfactory for the production of even moderately large quantities, a new method has been devised.

Methyl isobutyl ketone was obtained from ethyl isopropylacetacetate, and this, by reduction, was converted into methylisobutylcarbinol, which, by further reduction, yielded isohexane.

This procedure seems to be the best thus far devised for the production of isohexane, as the Wurtz method gives a very small yield, while the present one gives a yield of 57 per cent of the theoretical, reckoned from the carbinol, and about 37 per cent calculated from the ketone.

Incidentally, in the making of the carbinol, a small amount of pinacone was obtained, which was transformed into the corresponding dodecane, *viz.*, dimethyldiisobutylethane. Of the present series of hydrocarbons of established constitution, this, with the single exception of diisooctyl, is the first one above decane to be discovered which is not normal.[2]

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[1] Jahresb. d. Chem., 1855, p. 574.

[2] Alechin: J. russ. Chem. Soc., **15**, 175.

EXPERIMENTAL.

From ethyl acetacetate, ethyl isopropylacetacetate was prepared by Conrad's method,[1] from sodium ethyl acetacetate and isopropyl iodide. It boiled at 201°. The isopropyl iodide used was made by a modification of Markownikoff's method,[2] as follows: Two hundred grams of glycerin were mixed with 170 grams of water, 300 grams of iodine were added and, all at once, 60 grams of red phosphorus. The mixture was immersed in cold water for an hour, boiled with a return condenser over a free flame for 2 hours and distilled. The distillate was washed with water and with dilute sodium hydroxide solution, then with water again, and the colorless liquid dried with calcium chloride. On rectification it boiled at 89°. This method gave a consistent 70–80 per cent yield, reckoned from the glycerin.

Methyl Isobutyl Ketone.

This ketone has been prepared by Frankland and Duppa.[3] We modified their method and prepared it from ethyl isopropylacetacetate, by boiling for 6 hours with 10 per cent potassium hydroxide solution, 2 mol. alkali : 1 mol. ester. The resulting mixture was distilled with steam. The oily layer floating on the distillate was separated, dried over calcium chloride and fractionated. The fraction boiling between 100°–130° was 4 times redistilled, until a portion boiling at 119° (765 mm.) was obtained. Wagner[4] gives 115°.5 (745 mm.) and Frankland[5] 114° (758 mm.). Two hundred and forty-five grams of ethyl isopropylacetacetate yielded 89 grams of methyl isobutyl ketone, corresponding to 55 per cent of the theoretical. In addition to the boiling point,[5] the identity of this substance was further established by analysis.

I. 0.1052 gram substance gave 0.2790 gram CO_2 and 0.1043 gram H_2O.

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[1] Conrad and Limpach: Ann. Chem. (Liebig), **192**, 153.

[2] *Ibid.*, **138**, 364.

[3] Ann. Chem. (Liebig), **145**, 82.

[4] J. prakt. Chem., [2], **44**, 281.

[5] Ann. Chem. (Liebig), **145**, 83.

II. 0.1805 gram substance gave 0.4735 gram CO_2 and 0.1974 gram H_2O.

	Calculated for $C_6H_{12}O$.	Found. I.	Found. II.
C	72.00	72.43	71.60
H	12.00	11.01	12.15

The substance is readily miscible with alcohol, ether, benzene, acetone and ethyl acetate, but is insoluble in water.

Methylisobutylcarbinol.

This carbinol has been made from isovaleraldehyde and zinc methyl by Kuwschinoff.[1] We obtained it from methyl isobutyl ketone in the following manner: Seventy-five grams of methyl isobutyl ketone were dissolved in 150 grams of ethyl ether and the solution poured over 125 grams of water, contained in a round-bottom flask with a return condenser attached. To the mixture was added, piece by piece, 38 grams of sodium, during a period of 3 hours. The ether layer was then decanted, washed with water to remove a white turbidity and fractionated. The residue from the ether yielded two fractions, one boiling at 100°–150°, the other at 240°–245°. The first was methylisobutylcarbinol, the second methylisobutylpinacone.

The first fraction was twice distilled and gave 53 grams of methylisobutylcarbinol, boiling at 138°–145°, a yield of nearly 70 per cent of the theoretical. Analysis:

0.1540 gram substance gave 0.3959 gram CO_2 and 0.1853 gram H_2O.

	Calculated for $C_6H_{14}O$.	Found.
C	70.58	70.11
H	13.72	13.37

This compound has a peculiar odor like fusel oil. It is soluble in alcohol, ether, acetone, benzene, toluene, ethyl acetate and carbon tetrachloride; insoluble in water.

Ethylisobutyl.

This hexane has been prepared in the way already mentioned by Wurtz,[1] and extracted from gasolin by Norton and Andrews.[2] We obtained it from methylisobutylcarbinol by the following procedure: Fifty grams of the carbinol were dissolved in 70 cc. of redistilled amyl alcohol (b. p. 115°–125°, mostly near the lower figure) in a 500 cc. round-bottom flask, with a return condenser attached. Into this solution, cooled at 0°, was passed hydriodic acid gas, made from 88 grams of iodine,[3] after which 150 grams of glacial acetic acid were added, together with several pieces of granulated zinc. The mixture was allowed to stand 4 days, zinc being once added to keep it always present in excess; at the end of this time it was heated over the free flame and a fraction distilled off between 60° and 95°. This fraction will be described later.

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[1] J. russ. Chem. Soc., **19**, 205.

The residue from the distillation was treated with the hydriodic acid from 44 grams of iodine,[4] and more zinc, after which the mixture was allowed to stand again for 4 days. The distillation was repeated under the same conditions as before, the residue being treated with the same amount of hydriodic acid. This process was carried through 5 times. The product of the first distillation weighed 10 grams. This, on rectification, gave 1–2 cc. of hydrocarbons, derived from the amyl alcohol, boiling between 35° and 40°; 6 grams of isohexane, boiling at 64°, and a residue of amyl acetate and acetic acid. By the same treatment, the second distillate yielded 9 grams of rectified hexane; the third, 6.5 grams; the fourth, 7 grams; the fifth, 1.5 grams; and the sixth, 2.5 grams. The total yield of isohexane was 32.5 grams, but this contained nearly 3 per cent of iodine, although it boiled almost constantly at 62°–64°. By shaking with concentrated sulphuric acid and distilling, the iodine was removed entirely and a yield of 24 grams of isohexane obtained, corresponding to 57 per cent of the theoretical.

The success of this method seems to depend on the following facts: In the first place, the large amount of high-boiling solvents—amyl alcohol, amyl acetate and acetic acid—holds in solution the low-boiling hexane, and thus keeps it from evaporating during the several days of standing while the reduction is taking place. Secondly, the large amount of hydriodic acid transforms the methylisobutylcarbinol almost entirely to methylisobutyl iodide, and thereby gives the maximum amount of reducible material, since the carbinol cannot be reduced. Thirdly, the hydriodic acid aids in the evolution of hydrogen from the zinc. Fourthly, the excess of hydriodic acid adds to any hexylene which may be formed and, by transforming it into hexyl iodide, again brings it back into the sphere of action.

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[1] Jahresb. d. Chem., 1855, p. 574.

[2] THIS JOURNAL, 8, 6.

[3] Gatterman: "Pract. Meth. Org. Chem.," 2d Am. ed., p. 345.

[4] Gatterman: *Loc. cit.*

Methylisobutylpinacone.

The high-boiling fraction obtained as a by-product from the reduction of methyl isobutyl ketone, was twice distilled, the boiling point was 240°–255° the first time, but on redistillation it became constant at 245°. At ordinary temperatures it remained liquid.

The results of analysis and the method of formation show this compound to be a pinacone, with the formula,

$$(CH_3)_2CHCH_2C(CH_3)OHC(CH_3)OHCH_2CH(CH_3)_2.$$

Analysis:

0.1716 gram substance gave 0.4516 gram CO_2 and 0.1991 gram H_2O.

	Calculated for $C_{12}H_{26}O_2$.	Found.
C	71.28	71.62
H	12.87	12.87

Properties.—A viscous, oily liquid with a moderately strong odor like salt mackerel. It is soluble in alcohol, ethyl acetate, acetone, ethyl ether, benzene and glacial acetic acid; insoluble in water.

Reduction of Methylisobutylpinacone.

In a mixture of 10 grams of amyl alcohol (b. p. 116°–118°) and 40 grams of glacial acetic acid, 7 grams of methylisobutylpinacone were dissolved. Into this solution, cooled to 0°, was passed gaseous hydriodic acid from 44 grams of iodine,[1] and to it about 15 grams of zinc were added. The mixture was allowed to stand 5 days.

After this it was poured off from the remaining zinc into a flask with a side neck. On distilling over the free flame a few drops passed over at 70°–90° (hexane), while about one-half the total volume distilled at 100°–120°. On further heating, the temperature slowly rose to 170°, at which point the distillation was stopped. The residue was deep red in color. To the distillate was added 4 volumes of water, whereby a reddish colored oil separated out and sank to the bottom. This lower layer was drawn off, washed with water, dried with calcium chloride and distilled.

The first fraction distilled at 120°–135°, and consisted mainly of amyl acetate; the second boiled at 150°–170° and had an odor like an alkyl iodide, contaminated, however, by amyl acetate. To purify this second fraction, it was first washed with 60 per cent ethyl alcohol, then with pure water and finally dried with calcium chloride. On redistilling, it boiled almost constantly, but with some decomposition, at 158°–160° (760 mm.); 8 grams were obtained.

This compound is, undoubtedly, methylisobutylcarbinol iodide. The boiling point, 158°-160°, is what one would expect for such a substance, and it is easy to account for its formation from methylisobutylpinacone. The constitution, therefore, is $(CH_3)_2CHCH_2CHICH_3$. Analysis:

I. 0.2885 gram substance gave 0.3237 gram AgI.
II. 0.1138 gram substance gave 0.1265 gram AgI.

	Calculated for $C_6H_{13}I$.	Found. I.	Found. II.
I	59.87	60.63	60.07

Methylisobutylcarbinol iodide is a colorless, oily liquid, with the odor characteristic of alkyl iodides, it boils at 158°–160° with some decomposition and is insoluble in water, but dissolves in alcohol, ether and the common organic solvents.

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[1] Gatterman: *Loc. cit.*

Dimethyldiisobutylethane.

The residue in the flask, after distilling off the methylisobutylcarbinol iodide, was treated with 6 volumes of water. A thin oily layer, which floated on the water, was separated. It was dissolved in ligroin (b. p. 40°–70°) and the solution dried with calcium chloride. By distilling off the ligroin, a residue was obtained consisting of less than 1 cc. of colorless, oily liquid, which distilled at a little over 200°. By careful redistillation, the boiling-point 208°–210° was determined as accurately as possible with such a small quantity. Analysis:

0.1234 gram substance gave 0.3846 gram CO_2 and 0.1673 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found.
C	84.70	85.00
H	15.30	15.06

This analysis and the formation of the substance from methylisobutylpinacone show it to be the hydrocarbon, dimethyldiisobutylethane,

$$(CH_3)_2CHCH_2CH(CH_3)CH(CH_3)CH_2CH(CH_3)_2.$$

It is an oily liquid with a faint odor, soluble in ligroin but not very soluble in alcohol.

Contributions from the Chemical Laboratory of Harvard College.

ON THE ACTION OF CHLORIDE OF IODINE ON PYROCATECHIN.

BY C. LORING JACKSON AND M. C. BOSWELL.

The work described in this paper was undertaken in the hope of preparing tetraiodorthobenzoquinone, but none of the methods tried by us for making the tetraiodpyrocatechin have led to this substance. Of these, the action of monochloride of iodine on pyrocatechin seemed the most promising, because Michael and Norton[1] have found that this reagent converted resorcin into triiodresorcin, but our experiments with these two bodies showed that the reaction was by no means so simple as in the case of resorcin, since much iodine was set free, and red products obtained, which were evidently formed by the union of several molecules of pyrocatechin. We could find no way for purifying these substances directly, but by reducing them with sulphurous dioxide, after the removal of the iodine, we succeeded in obtaining two white compounds, one melting at 224°, when a small proportion of the ICl had been used (10 : 90 ICl), the other melting at 252°, formed by a larger amount (10 : 120 ICl). Preliminary experiments indicated that still another compound, at least, could be obtained by varying the proportion of chloride of iodine, but that variations in the other conditions seemed to have no effect on the product.

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[1] Ber. d. chem. Ges., 9, 1752 (1876).

Our analytical results with the substance melting at 224° leave us in doubt as to which of two formulas belongs to it, $C_{30}H_{19}O_{10}Cl_8I_3$ or $C_{26}H_{18}O_9Cl_7I_2$; the balance of evidence is in favor of the first, but it is impossible to decide between them by analysis alone, and our only analysis of a derivative, that of the acetyl compound, although declaring in favor of the first formula, is not absolutely decisive. We were unable to settle this point because our work was broken off before it was finished by the departure of one of us from Cambridge. Either of the compounds represented by these formulas might have been formed by the reaction, since the first consists of 5 molecules of pyrocatechin, in which part of the hydrogen has been replaced by the halogens, the second of 4 molecules of pyrocatechin, in which part of the hydrogen has been replaced by the halogens and an acetyl group. The hydrogen given in these formulas is the maximum amount, but it is probable that some of it has been eliminated in the process of uniting the molecules of pyrocatechin.

The supposition that a molecule containing 5 benzene rings would crystallize well and melt as low as 224° seems, at first sight, very improbable, but it is not without analogy in this class of compounds, as a derivative of tetrachlororthoquinone has been prepared by Mr. MacLaurin in this laboratory, which, [illegible] shown by molecular weight determinations, contains 4 benzene rings and melts at 210°.

As to the constitution of our octochlortriiodpentapyrocatechin, much more work will be necessary before it can be definitely settled, but we have established the following points with tolerable certainty: Oxidation with nitric acid converts it into a red substance, melting at 272°, crystallizing with toluene of crystallization, and acted on by most solvents. There can be little doubt, therefore, that it is an orthoquinone, probably the same as the dark red first product of the action of ICl on pyrocatechin. In that case the compound melting at 224° must contain two hydroxyl groups in the ortho position. Further, if in preparing this substance the reduction with sulphurous dioxide is carried on without removing the free iodine, the product is trichlorpyrocatechin, undoubtedly due to the decomposition of the octochlor body by the hydriodic acid, which indicates that our substance contains one group $C_6HCl_3O_2$ at least. As has been already pointed out, it is probably analogous to the polymeric derivative of substituted orthoquinone discovered by Mr. MacLaurin, which it resembles closely in many properties.

The substance melting at 252°, obtained with a larger amount of ICl, gave analytical results agreeing with the formula $C_{18}H_{10}O_6Cl_7I$, and analysis of the acet derivative gave results also in agreement with this formula, but other derivatives should be analyzed before its composition is considered finally settled. Such a compound would be made up of three pyrocatechin molecules with part of the hydrogen replaced by the halogens, and therefore should be called heptachloriodtripyrocatechin. It is certainly strange that this tripyrocatechin compound melts at a higher temperature than the pentapyrocatechin compound, but this may be accounted for by the greater replacement of hydrogen by halogens in the former than in the latter.

If the tripyrocatechin is oxidized with nitric acid, it gives a red compound, probably an orthoquinone; and if, in preparing it, the reduction with sulphurous dioxide is carried on before the iodine has been removed, tetrachlorpyrocatechin is formed, which crystallizes from water with 1 H_2O. The formula of the tripyrocatechin may, therefore, be developed as follows:

$$C_6Cl_4O_2(C_{12}H_8Cl_3IO_2)O_2H_2.$$

Consequently, our experiments show that the action of monochloride of iodine on pyrocatechin leads to the union of several molecules of it, for in no case did we obtain derivatives from a single molecule, except where, by reduction with sulphurous dioxide and hydriodic acid, the trichlor or tetrachlorpyrocatechin was obtained, and in view of all the facts observed these must have been formed by the breaking up of the more complex real products of the reaction. We ascribe this greater complexity of the reaction to the formation of orthoquinones, which have a great tendency to form such complex aggregates. That such quinones were formed was shown by the red color of the products and confirmed by the fact that much iodine was set free. The introduction of chlorine as well as iodine into the molecule is another marked difference between the action of chloride of iodine on pyrocatechin and on resorcin or aniline.

Many other methods for making tetraiodpyrocatechin or orthoquinone were tried, but none of them led to the desired result.

EXPERIMENTAL.

Action of Monochloride of Iodine on Pyrocatechin.

The chloride of iodine, ICl, used by us was made by passing washed and dried chlorine into a flask containing a weighed quantity of iodine, until the calculated amount of chlorine had been taken up, as shown by the increase of weight. This point was also indicated by the appearance of yellow crystals of the tetrachloride of iodine.

Compound Melting at 224°.—Thirty grams of pyrocatechin were dissolved in 900 cc. of glacial acetic acid and treated with 270 grams of monochloride of iodine, introduced by passing a stream of air through the flask containing it, which was heated on the water-bath to 50°–60°. A precipitate of iodine was formed during the addition of the chloride and, after the required amount had been introduced, the dark colored liquid was poured off from this iodine and heated for an hour on the steam-bath, with vigorous shaking at intervals of 10 minutes, when large quantities of hydrochloric acid were given off. Three or four liters of water were then added to the product, which precipitated a dark colored mass containing a great deal of iodine. This was next removed by rubbing it with a strong solution of potassic iodide and washing with water. The dark red residue could not be purified by any solvents which we could find, since they either converted it into light colored products, as in the case of dilute acetic acid or alcohol, or, if there was no chemical action, the solutions yielded no crystals. Accordingly, we proceeded as follows: The substance was dissolved in glacial acetic acid with the aid of a gentle heat, and a stream of sulphurous dioxide was passed through the solution, until a sample gave a white precipitate with water. The whole was then diluted and the solid thus obtained crystallized three times from alcohol, when it showed the constant melting point 224°, and was dried at 100° for analysis.

I. 0.3049 gram substance gave 0.3551 gram CO_2 and 0.0309 gram H_2O.

II. 0.3093 gram substance gave 0.3512 gram CO_2 and 0.0615 gram H_2O.

III. 0.2078 gram substance gave 0.2379 gram CO_2 and 0.0535 gram H_2O.

IV. 0.1892 gram substance gave 0.2883 gram AgCl + AgI, which yielded 0.2193 gram Ag_2S.

V. 0.1759 gram substance gave 0.2693 gram AgCl + AgI.

VI. 0.3191 gram substance gave 0.4875 gram AgCl + AgI.

	I.	II.	III.	IV.	V.	VI.
C	31.76	30.96	31.22	. .	. .	. .
H	1.18	2.21	2.86	. .	. .	. .
Cl_8[1]	. .	. .	. .	23.35	23.46	23.41
I_3	. .	. .	. .	31.32	31.47	31.41

The analyses were made with specimens from more than one preparation.

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[1] These results were calculated on the supposition that there are Cl_8I_3 in the compound. The proportion Cl_7I_2 is also possible; in that case the results become:

	IV.	V.	VI.
Cl_7	25.68	25.81	25.75
I_2	26.25	26.38	26.32

The determination of the relative amounts of chlorine and iodine was based on the conversion of the precipitate of AgCl + AgI into argentic sulphide by the following method: The precipitate, after it had been weighed on a Gooch crucible, was shaken with the asbestos mat into a beaker and treated with a cold, strong solution of sodic thiosulphate, the crucible being washed with a portion of a similar solution. After all the silver salts had been dissolved in this way, ammonic sulphide was added, the mixture allowed to stand over night and the Ag_2S dried at 110° on a Gooch crucible.

This indirect determination is so unfavorable that several different proportions of chlorine and iodine give results agreeing with the amount of argentic sulphide obtained, but when the other analytical numbers are brought into the calculation, only two proportions are found to be possible—Cl_8I_3 and Cl_7I_2.

Weights of Ag_2S Corresponding to 0.2883 Gram AgCl + AgI (Analysis IV.).

Calculated for		
8AgCl + 3AgI.	7AgCl + 2AgI.	Found.
0.2122	0.2183	0.2193

The second proportion agrees excellently with the experimental result, but the first, although not so good, is not far enough out to be rejected.

The two formulas derived from these proportions of the halogens give percentages which are compared with those from Analyses III. and VI. in the following table:

	Calculated for		
	$C_{30}H_{19}O_{10}Cl_8I_3$.	$C_{26}H_{18}O_9Cl_7I_2$.	Found.
C	29.90	31.37	31.22
H	1.58	1.81	2.86
Cl_8	23.59	. .	23.41
I_3	31.64	. .	31.41
Cl_7	. .	25.00	25.75
I_2	. .	25.54	26.32

These results point to the formula $C_{30}H_{19}O_{10}Cl_8I_3$ as the correct one, although the C is over 1 per cent too high for it, but in the presence of so much halogen this result is more probable than that according to Formula II., as this, in spite of the greater apparent agreement, requires more carbon than was found. The percentages from Analysis I., to be sure, agree with the second formula, but the low hydrogen and high carbon in this analysis are so improbable that we feel inclined to reject it.

An acetyl derivative was made by heating the compound melting at 224° with a large excess of acetyl chloride on the steam-bath, for half an hour. The product was then precipitated with water, purified by recrystallization from dilute alcohol, and dried at 100°.

0.2115 gram substance gave 0.3160 gram AgCl + AgI.

	Calculated for $C_{30}H_{17}O_{10}(C_2H_3O)_2Cl_8I_3$.	Found.
Cl_8	22.05	22.90
I_3	29.57	30.72

	Calculated for		Found.
	$C_{26}H_{16}O_9(C_2H_3O)_2Cl_7I_2$.	$C_{26}H_{17}O_9C_2H_3OCl_7I_2$.	
Cl_7	23.04	23.98	25.19
I_2	23.55	24.51	25.74

These results, although they leave much to be desired, agree best with $C_{30}H_{19}O_{10}Cl_8I_3$ as they stand, but the following considerations make them tell even more strongly in its favor. The white compound, melting at 224°, when oxidized with nitric acid, was converted into a red body melting at 272°, which showed the properties of an orthoquinone. The original substance was, therefore, probably the corresponding pyrocatechin, which, on treatment with acetyl chloride, would give a diacet body. If this supposition is true, the analysis is decisive in favor of Formula I., but, even if it is not, the evidence at hand is so strong for this formula, $C_{30}H_{19}O_{10}Cl_8I_3$, that it can be adopted, until further work has furnished decisive results. Such a compound would be made up of 5 molecules of pyrocatechin with part of the hydrogen replaced by chlorine and iodine. A substance having Formula II. would be made up of 4 molecules of pyrocatechin, in which part of the hydrogen was replaced by chlorine, iodine and one acetyl group; both, therefore, are compounds which might have been formed under the conditions of the reaction. The maximum amount of hydrogen is assumed to be present in these formulas; obviously a less amount might be nearer the truth.

If the formula $C_{30}H_{19}O_{10}Cl_8I_3$ is adopted for the substance melting at 224°, it would be called octochlortriiodpentapyrocatechin. It crystallizes from somewhat dilute alcohol in long, silky, white needles, which melt at 224° and are soluble in ether, benzene, or acetic acid. With nitric acid it is converted into a dark red substance (probably identical with the direct product from the action of chloride of iodine on pyrocatechin), which is very slightly soluble in the common solvents ; but we succeeded in obtaining it from toluene in long, bright red needles, which grew darker on drying, probably from loss of toluene of crystallization, and then melted[1] at 272°. It showed a tendency to turn light yellow when treated with benzene, ligroin, or dilute acetic acid. These properties indicate that it is an orthoquinone.

Trichlorpyrocatechin.

In the process given for preparing octochlortriiodpentapyrocatechin, if the iodine was not removed from the crude product before the reduction with sulphurous dioxide, a different result was obtained, as shown by the following experiment, which was repeated several times : Thirty grams of pyrocatechin were dissolved in 500 cc. of glacial acetic acid and treated with 280 grams of chloride of iodine, either passed into the solution in a current of air or added in solution in acetic acid. The mixture, after standing over night, was heated on the steam-bath for half an hour and then treated with sulphurous dioxide and a little water (not enough to form a precipitate) until it was decolorized, when 1.5 liters of water were added and the voluminous, white precipitate, formed on stirring and cooling with ice, filtered out and purified by crystallization from hot water. Instead of melting at 224° this product melted at 115° and, after drying at 70°, at 134°–135°. This indicated that it might be the trichlorpyrocatechin, which, according to Cousin,[2] melts, when dried, at 134°–135°, but at 104°–105° with its water of crystallization. We are unable to explain this difference of 10° between our melting point and that of Cousin. The following analyses prove that it is this substance :

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[1] This melting point is subject to revision by later experiments on a larger scale.

[2] Bull. Soc. Chim., [3], 13, 719. Ann. Chim. Phys., [7], 13, 483.

I. 1.1008 grams air-dried substance lost 0.0891 gram, when dried at 100°, but this loss was accompanied by decomposition, shown by the darkening of the specimen. This decomposition by heat was also observed by Cousin.

II. 0.3232 gram air dried substance gave 0.3641 gram CO_2 and 0.0549 gram H_2O.

III. 0.3102 gram substance gave 0.3557 gram CO_2 and 0.0723 gram H_2O.

IV. 0.2079 gram substance gave 0.3836 gram AgCl, which yielded 0.3325 gram Ag_2S instead of 0.3315 gram.

V. 0.2334 gram substance gave 0.4319 gram AgCl, which yielded 0.3710 Ag_2S instead of 0.3733 gram.

There can be no doubt, therefore, that the substance contained chlorine and no iodine.

	Calculated for $C_6HCl_3(OH)_2.H_2O$.	Found.				
		I.	II.	III.	IV.	V.
H_2O	7.78	8.10	. .	. .	. .	. .
C	31.11	. .	30.70	31.27	. .	. .
H	2.16	. .	1.89	2.59	. .	. .
Cl	46.02	. .	. .	. .	45.61	45.75

As this trichlorpyrocatechin was obtained by the method, which gave the octochlortriiodpentapyrocatechin, when the iodine was removed before reduction, it must owe its formation to the action of hydriodic acid and there can be little doubt that this consists in breaking up the complex molecule of the substance melting at 224°. If the reduction with sulphurous acid and hydriodic acid was long continued, water precipitated nothing from the acetic acid solution.

Compound Melting at 252°.—When, in treating pyrocatechin with chloride of iodine, the proportion of this reagent was raised from 135 grams to 180 grams for 15 grams of pyrocatechin ; the other conditions remaining the same, a different compound was obtained which, after crystallization from hot, dilute alcohol, showed the constant melting point 252°, and, when dried at 100°, gave the following results on analysis :

I. 0.2720 gram substance gave 0.3085 gram CO_2 and 0.0363 gram H_2O.

II. 0.3133 gram substance gave 0.3595 gram CO_2 and 0.0763 gram H_2O.

III. 0.2259 gram substance gave 0.4046 gram AgCl + AgI, which yielded 0.3273 gram Ag_2S.

IV. 0.2318 gram substance gave 0.4150 gram AgCl + AgI, which yielded 0.3385 gram Ag_2S.

	Calculated for $C_{18}H_{10}O_6Cl_7I$.	Found.			
		I.	II.	III.	IV.
C	30.97	30.93	31.30	. .	. .
H	1.43	1.48	2.71	. .	.
Cl	35.63	. .	. .	35.91	35.90
I	18.21	. .	. .	18.35	18.34

The 0.4046 gram of AgCl + AgI (Analysis III.) gave 0.3273 gram Ag_2S. 7AgCl + AgI give 0.3238 gram Ag_2S.

0.4150 gram AgCl + AgI (Analysis IV.) gave 0.3385 gram Ag_2S. 7AgCl + AgI give 0.3321 gram Ag_2S.

The acetyl derivative was also made by boiling with an excess of acetyl chloride for half an hour, precipitating with water and purifying by crystallization from hot, dilute alcohol. After drying at 100° it gave the following result:

0.1541 gram substance gave 0.2505 gram AgCl + AgI.

	Calculated for $C_{18}H_8O_6(C_2H_3O)_2Cl_7I$.	Found.
Cl	31.80	32.60
I	16.25	17.65

A substance with the formula $C_{18}H_{10}O_6Cl_7I$ would be formed by the union of 3 molecules of pyrocatechin, in which part of the hydrogen had been replaced by the chlorine and iodine. The amount of hydrogen given is the maximum, but there may be a smaller quantity present. This heptachloriodtripyrocatechin crystallizes from hot, somewhat dilute alcohol in long, fine, white, silky needles, which melt at 252° and are less soluble in alcohol or acetic acid than the octochlor compound.

Tetrachlorpyrocatechin.

Fifteen grams of pyrocatechin were dissolved in 800 cc. of glacial acetic acid and treated with 180 grams of chloride of iodine, introduced by means of a current of air, the liquid was then poured off from a quantity of iodine, that had been deposited, heated on the steam-bath, decolorized with sulphurous dioxide and water, and finally diluted with a large volume of water. At first there was no precipitate, but on standing over night long, white needles were formed, which melted at 193°–194° ; tetrachlorpyrocatechin melts at 194°–195°. This preparation should have given heptachloriodtripyrocatechin, if the iodine had been removed before reducing with sulphurous dioxide. That the substance is tetrachlorpyrocatechin was proved by the following analysis :

0.2156 gram air-dried substance gave 0.4670 gram AgCl, which yielded 0.4007 gram Ag_2S instead of 0.4035 gram. The silver salt is, therefore, AgCl.

	Calculated for $C_6Cl_4(OH)_2.H_2O$.	Found.
Cl	53.38	53.56

Tetrachlorpyrocatechin as prepared by Zincke[1] and by Zincke and Küster[2] was anhydrous, since it was crystallized from glacial acetic acid. We, accordingly, determined the amount of water of crystallization in our preparation :

0.6825 gram air-dried substance lost 0.0424 gram when dried at 110°.

	Calculated for $C_6Cl_4(OH)_2.H_2O$.	Found.
H_2O	6.77	6.21

If in this reduction with sulphurous dioxide, in presence of iodine, the reducing action is long continued, water precipitates nothing from the product.

The conditions under which the chloride of iodine acted on the pyrocatechin were varied in many ways, but the only variations which seemed to affect the product were in the proportion of the two reagents and the nature of the solvent. The concentration of the solution had no effect, unless it was so great that the reaction became too violent, producing decomposition. Temperatures from 0° to 100° did not modify the product, but it was found that the reaction ran very slowly below 60°. The chloride of iodine could be introduced indifferently in a stream of air, in solution in acetic acid, or directly from a drop funnel. When water or chloroform replaced the acetic acid as the solvent, the product was tarry and gave, with benzene and ligroin, reddish brown crystals, which seemed to be different from those obtained with acetic acid.

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[1] Ber. d. chem. Ges., **20**, 1779 (1887).

[2] *Ibid.*, **21**, 2729 (1888).

As already shown, different proportions of chloride of iodine gave different products, and we have reason to suppose that several other substances might be obtained by varying these proportions still further. This was indicated by the following preliminary experiments: Five grams of pyrocatechin, dissolved in 85 cc. of acetic acid, were treated with 75 grams of chloride of iodine (a much larger excess than any used above) and allowed to stand 3 days, precipitated with water and, after 3 hours, the deposit filtered out and recrystallized from alcohol, when it showed the melting point 270°. Perhaps the same substance was obtained from the alcoholic mother liquors in purifying the product melting at 252°. The aqueous filtrate, in the preparation described above, also seemed to contain another substance.

A solution of 2.5 grams of pyrocatechin in 15 cc. of acetic acid was added, very slowly, to a solution of chloride of iodine in about 3 times the amount of acetic acid, and heated on the steam-bath. Much iodine was precipitated and the hot liquid poured off from this deposited beautiful needles, which turned white after washing with potassic iodide. This product differed from all the others in being unaffected by nitric acid, while the others are reddened by oxidation. We tried many times to prepare this substance again, but without success.

After we were convinced that tetraiodpyrocatechin could not be made with chloride of iodine acting on pyrocatechin, the following unsuccessful experiments were tried with other processes: Iodine was allowed to act on pyrocatechin either alone or with iodic acid, plumbic oxide, or mercuric oxide, in solution in water, alcohol, ether, or acetone, cold or hot, but without any formation of tetraiodpyrocatechin. With iodic acid the pyrocatechin was charred; with the metallic oxides there was no action. Fuming sulphuric acid and iodine decomposed the pyrocatechin. Tetrachlorpyrocatechin, in alcoholic solution, was boiled for 2 days with potassic iodide, without action. Pyrocatechin diacetate gave, with chloride of iodine, the same results as pyrocatechin itself.

CAMBRIDGE, MASS.,
March 20, 1906.

THE COMBUSTION OF HALOGEN COMPOUNDS IN PRESENCE OF COPPER OXIDE.

BY CHARLES J. ROBINSON.

In the course of some work by J. Bishop Tingle and the author of this note, occasion arose for determining carbon and hydrogen in certain compounds containing a halogen, and an attempt was made to do away with the necessity for preparing a combustion tube filled with lead chromate by suitably modifying the ordinary tube containing copper oxide. This purpose was accomplished simply and satisfactorily in the following manner:

A cartridge, similar to that employed by Morse and Taylor[1] in the analysis of sulphur compounds, was made by rolling a small piece of heavy copper wire gauze into the form of a hollow cylinder, which was only 6 or 7 cm. long, and just fitted into the combustion tube. The cylinder was filled with pure lead chromate, the ends closed by wrapping with copper wire, which also passed lengthwise through the cartridge, and was looped at each end to facilitate removal from the tube. The copper parts were oxidized by ignition. When it was desired to analyze halogen compounds, this cartridge was placed just in front of the boat, in a combustion tube filled in the ordinary way with copper oxide. In burning, care was taken that the part of the tube containing the cartridge was well heated before decomposition of the substance began, but no other special precautions were found necessary. If the space in the tube, or the decomposition temperature of the substance to be analyzed demand it, the oxidized spiral in front of the boat should, of course, be removed and the cartridge be allowed to occupy its place.

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[1] THIS JOURNAL, 33, 602.

The advantages gained by the use of this device are that combustions of halogen compounds can be made just as readily as combustions of ordinary compounds, and that the same tube can be used for both. The cartridge may be removed or not, as the operator pleases, to make ordinary analyses subsequent to analyses of substances containing halogens. The same cartridge may be used repeatedly, but no statement can be made as to the number of times it can be employed safely without renewal, because of the great variation in content of halogen in different compounds. The life of the tube itself is not affected as it is when the tube is entirely filled with lead chromate.

The method has been found to be so completely satisfactory that it is judged decidedly preferable, in very many cases, to determine carbon and hydrogen rather than halogen for the identification of new compounds. The time required for the analysis is much shorter, and the figures for the content of carbon and hydrogen in complex bodies are usually much more distinctive than those for the content of halogen.

No special experiments have been conducted to test the method, but the analyses given below were made in the course of the investigation referred to. The substances analyzed are products of the action of *p*-bromphenylhydrazine on camphoroxalic acid. Only the one determination of carbon and hydrogen was made in each case.

I. A compound $C_{18}H_{23}O_4N_2Br$, melting at 149° with decomposition.

0.2409 gram substance gave 0.4603 gram CO_2 and 0.1150 gram H_2O.

	Calculated.	Found.
C	52.53	52.14
H	5.63	5.34

II. A compound $C_{18}H_{21}O_3N_2Br$, melting at 172° with decomposition.

0.2135 gram substance gave 0.4308 gram CO_2 and 0.0982 gram H_2O.

	Calculated.	Found.
C	54.94	55.03
H	5.38	5.15

III. A compound $C_{20}H_{23}O_2N_2Br$, m. p. 107°.

0.2125 gram substance gave 0.4624 gram CO_2 and 0.1045 gram H_2O.

	Calculated.	Found.
C	59.52	59.35
H	5.75	5.50

IV. A compound, $C_{18}H_{19}O_2N_2Br$, melting at 215° with decomposition.

0.1937 gram substance gave 0.4095 gram CO_2 and 0.0923 gram H_2O.

	Calculated.	Found.
C	57.58	57.66
H	5.10	5.33

The method has also been applied to the determination of nitrogen in halogen compounds. The cartridge of lead chromate is placed just in front of the substance to be burned, and the latter is mixed with lead chromate. Otherwise the tube is filled in the ordinary way with copper oxide. The results obtained are shown in the following analysis:

I. The compound $C_{18}H_{21}O_3N_2Br$.

0.2624 gram substance gave 16.2 cc. N_2 at 19° and 758 mm.

	Calculated.	Found.
N	7.14	7.08

The determination of carbon and hydrogen in sulphur compounds could, doubtless, be accomplished in the same manner, in the presence of copper oxide, but no experiments have been made in this direction.

JOHNS HOPKINS UNIVERSITY,
April, 1906.

OBITUARY.

PIERRE CURIE.

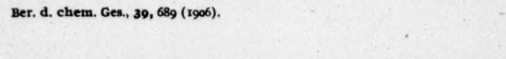
Professor Pierre Curie was born May 15, 1859, and was knocked down and killed by a wagon in Paris, April 19, 1906. Curie received his education in Paris and in 1895 obtained the degree of Doctor of Science from the University there. At the time of his death he was professor of general physics at the École Municipale de physique et de chimie industrielles, professor of physics in the Faculty of Sciences, University of Paris, and member of the Académie des Sciences of the Institute of France. He was also an honorary member of various foreign scientific societies. This is not the place to detail Curie's purely physical work; to chemists he is best known by his researches in the field of radio-activity. His earliest paper on this subject appeared in 1898; it was written in conjunction with Madame Curie and led her to the discovery of polonium and radium. Curie was the first to observe that radium constantly evolves heat and he measured its amount. He also showed that the radiations of radium consist of two kinds; he determined the emanating power of radium compounds and, following Ramsay, proved that helium is produced from radium.

REPORTS.

A New Oxide of Carbon, C_3O_2. Carbon Suboxide.

What is, in many respects, one of the most interesting discoveries which has been made for several years, has recently been announced from E. Fischer's laboratory by Otto Diels and Bertram Wolf.[1] By the action of phosphorus pentoxide on ethyl malonate vapor at about 300°, in an apparatus of special construction, they have succeeded in obtaining an anhydride of malonic acid.

In view of what is known of the action of phosphorus pentoxide on esters, one or the other of the following equations must represent its action on ethyl malonate:



$$CH_2(CO_2C_2H_5)_2 \longrightarrow 2C_2H_4 + H_2O + CH_2\left<\begin{matrix}CO\\CO\end{matrix}\right>O\ ;$$

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[1] Ber. d. chem. Ges., 39, 689 (1906).

$$CH_2(CO_2C_2H_5)_2 \rightarrow 2C_2H_4 + 2H_2O + OC : C : CO.$$

That the new compound is formed according to the second equation is proved by its vapor density, composition and properties.

Carbon suboxide is a colorless, highly refractive, volatile liquid, which boils at 7° and has an odor resembling that of acrolein and oil of mustard. It rapidly attacks the eyes, throat and respiratory organs and, when breathed in quantity, produces symptoms of suffocation.

Chemically, carbon suboxide acts essentially as an anhydride of malonic acid, but it also exhibits certain affinities to the carbonyl compounds such as $Ni(CO)_4$ and $Fe(CO)_5$[1] and is to be regarded as carbon carbonyl. It burns with a very smoky, intensely blue flame and reacts rapidly with water to form malonic acid; with dry hydrogen chloride malonyl chloride is formed, while aniline and ammonia yield malonanilide and malonamide, respectively.

Carbon suboxide decomposes spontaneously at 15°, in the course of a day or two; the liquid becomes yellow, deposits a solid, darkens and finally is completely transformed into a dark red solid. This readily dissolves in water with an eosin-red color.

At 37° the transformation of the carbon suboxide is much more rapid, the product being very hard, and deep black-red in color. In part it dissolves in water, giving a dark brown solution. At 100° the decomposition of carbon suboxide is instantaneous. These decomposition products are probably similar to the compounds C_4O_3 and C_8O_3, or, possibly, they are identical with them. The two substances in question were described by Brodie and by Berthelot about 30 years ago; the former was prepared by the action of a silent electric discharge on carbon monoxide and the latter by heating C_4O_3.

J. BISHOP TINGLE.

Amino Acids, Polypeptides and Proteids.

In a lecture given recently before the German Chemical Society, Emil Fischer[2] summarizes the results obtained from the researches which he has carried out on the above substances during the past 6 years. His work began with a study of the amino acids; at that time only 9 monamino acids, 3 diamino acids, and cystine, which contains sulphur, had been recognized as decomposition products of proteids; 8 racemic modifications of these monamino acids had been synthesized.

The two most general practical methods which were known were the action of ammonia on α-halogen aliphatic acids and that of ammonia and hydrogen cyanide on an aldehyde. Fischer has improved the former method by brominating alkyl malonic acids, obtaining $RCBr(COOH)_2$, which, when heated, yields a brom aliphatic acid. Among other important compounds, α-aminocaproic acid (leucine),

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[1] THIS JOURNAL, 35, 469 (1906).
[2] Ber. d. chem. Ges., 39, 530 (1906).

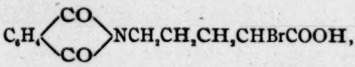
$$CH_3CH_2CH_2CH_2CH(NH_2)COOH,$$

was prepared by this method.

With the exception of glycocoll, all the amino acids obtained from proteids contain an asymmetric carbon atom and are optically active, but the synthetical products are, of course, racemic. Fischer's method of resolving these latter is beautifully simple; the benzoyl or formyl derivatives are prepared; these are strong acids, their salts with optically active bases can readily be separated by crystallization and the optically active form of the original acid may then be obtained by hydrolysis. The list of optically active acids prepared in this manner is already lengthy and includes α-aminopropionic acid (alanine), $CH_3CH(NH_2)COOH$, α-aminocaproic acid (leucine), $CH_3CH_2CH_2CH_2CH(NH_2)COOH$, β,*p*-hydroxyphenyl-α-aminopropionic acid (tyrosine),

$$HOC_6H_4CH_2CH(NH_2)COOH, \text{ etc.}$$

The synthesis of the diamino acids is a much more difficult problem than the preparation of monamino acids. Fischer has introduced marked improvements into two of the existing methods. The following example will serve to illustrate the first one: Ethyl phthaliminopropylmalonate readily yields a brom derivative which, when hydrolyzed and heated, gives phthaliminobromovaleric acid,



$$C_6H_4\begin{cases}CO\\CO\end{cases}\!\!>NCH_2CH_2CH_2CHBrCOOH,$$

by the action of ammonia and the removal of the phthalyl group α,δ-diaminovaleric acid,

$$H_2NCH_2CH_2CH_2CH(NH_2)COOH,$$

is formed. A better method for obtaining acids of this class depends on the action of nitrous acid on cyanalkyl malonates thus:

$$NCCH_2CH_2CH_2CH(COOC_2H_5)_2$$

yields

$$NCCH_2CH_2CH_2C(NOH)COOC_2H_5,$$

which, when reduced by means of sodium and alcohol, yields α,ϵ-diaminocaproic acid (racemic lysine),

$$H_2NCH_2CH_2CH_2CH_2CH(NH_2)COOH.$$

A third method consists in the addition of ammonia to acids containing 2 ethylene linkages.

The hydroxyamino acids having also been found in the decomposition products of proteids, it became necessary to improve the available means of obtaining them synthetically. Fischer found that Strecker's method, consisting in the combined action of ammonia and hydrogen cyanide, could be applied to the hydroxy aldehydes, the resulting cyanhydrin being then hydrolyzed. In this manner α-amino-β-hydroxypropionic acid (serine), $HOCH_2CH(NH_2)COOH$, was prepared from glycollic aldehyde. The same reactions have also been used to obtain certain derivatives of galactose and arabinose.

An extensive study had to be made of various derivatives of the amino acids in order to devise new processes for their isolation, recognition, purification, separation and condensation, and attention was naturally directed to the acyl derivatives. Although hippuric acid is readily obtained from aminoacetic acid, benzoyl chloride and sodium hydroxide, this method is not applicable to the majority of amino acids, but the use of sodium bicarbonate instead of the hydroxide frequently gives good results. Formyl derivatives can be obtained even more readily by boiling the amino acid with anhydrous formic acid. The use of these acyl derivatives for the resolution of racemic compounds has been mentioned above. Acetyl derivatives are not very satisfactory, but benzenesulphonic chloride and, particularly, β-naphthalenesulphonic chloride have proved to be of great value in the separation of mixtures of amino acids, unfortunately, however, the resulting sulphonyl derivatives are only hydrolyzed with difficulty. Phenylisocyanate and α-naphthylisocyanate frequently yield derivatives of the amino acids which crystallize readily.

The first important work on the esters of amino acids was done by Curtius, who demonstrated their ease of formation by the action of alcohol and hydrogen chloride, and studied a few of their reactions. Fischer found that many of these esters could be readily isolated from the ester hydrochlorides by the action of alkali, at low temperatures, and that the free esters thus obtained could be employed for the separation and purification of the amino acids, partly on account of differences in boiling point under greatly reduced pressure, partly from their varied solubility. These esters, unlike the acids, have basic properties only and are highly reactive, derivatives have been obtained of some of them with acid chlorides, anhydrides, halogen alkyls, isocyanates, alkylthiocarbimides (mustard oils), aldehydes, ketones, carbon bisulphide, carbonyl chloride and ammonia. Certain of these compounds are of considerable interest, but of even greater importance was the preparation of the chlorides of such amino acids, because these chlorides could be used in the synthesis of polypeptides. After many unsuccessful efforts, it was found that the desired result could be obtained by the action of phosphorus pentachloride, in acetyl chloride solution, on the finely divided acid hydrochloride. This reaction has only been applied to acids with one amino and one carboxyl group; it has uniformly succeeded with them, but, oddly enough, it fails absolutely with aminoacetic acid which has been crystallized from water, no matter how completely the acid may be subsequently powdered and dried. The products have the formula $RCH(NH_2Cl)COCl$. Diamino and hydroxyamino acids give phosphorus derivatives under the above conditions.

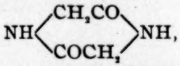
Fischer gives, in some detail, the processes he has found to be of most service in the separation of individual acids from mixtures. The first step is to esterify, by the method already referred to, and then to fractionate under greatly reduced pressure, down to 0.5 mm. This not only effects a fairly good separation of individual esters, but serves to remove inorganic substances, complicated amino and hydroxyamino acids and polypeptides. The individual fractions are then further differentiated by means of their own varied solubility, by that of the free acids, by the use of phenylisocyanate, or by the preparation of naphthalenesulphonic acid derivatives, etc. The diamino acids, as is well known, are usually separated by means of phosphotungstic acid, but this method must be used with care or they will be contaminated by monoamino compounds. The first section of the lecture concludes with a summary of the methods of separation used for more than 30 of the more important compounds, together with full references to the literature.

The second part of the lecture is devoted to the polypeptides, *i. e.*, amide derivatives of amino acids. The simplest representative of this class of substances is glycylglycine,

$$H_2NCH_2CONHCH_2COOH\ ;$$

the prefixes di, tri, tetra, etc., indicate the number of acid radicles present in any such compound. The term "peptide" is derived from peptone. Fischer regards his synthetic polypeptides as very closely related to natural peptones, indeed he believes that these latter consist, essentially, of mixtures of polypeptides.

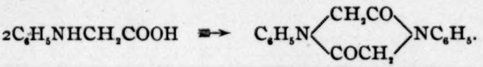
The synthetical products allied to polypeptides, which had been obtained before Fischer began his work, were amorphous and poorly characterized. Curtius' open chain compounds were well defined and crystalline, but they all contained the benzoyl group; however, he succeeded in obtaining the simplest diketopiperazine,



$$NH\left\langle\begin{matrix}CH_2CO\\COCH_2\end{matrix}\right\rangle NH,$$

from ethyl aminoacetate, a matter of great importance for the chemistry of the dipeptides. The following synthetical methods have been employed in Fischer's work, some have been devised by him, others were already known:

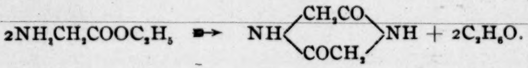
(*I*) *Synthesis of Polypeptides from Diketopiperazines. Synthesis of Diketopiperazines.* — (i) Dehydration of amino acids by heating them in a current of carbon dioxide or hydrogen chloride:



$$2C_6H_5NHCH_2COOH \rightarrow C_6H_5N\left\langle\begin{matrix}CH_2CO\\COCH_2\end{matrix}\right\rangle NC_6H_5.$$

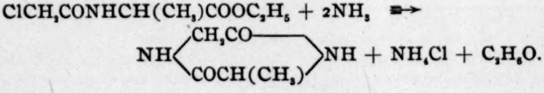
Diphenyldiketopiperazine.

(ii) Transformation of the esters of amino acids in aqueous solution:



$$2NH_2CH_2COOC_2H_5 \rightarrow NH\left\langle\begin{matrix}CH_2CO\\COCH_2\end{matrix}\right\rangle NH + 2C_2H_6O.$$

(iii) The action of ammonia on the esters of amino acids which contain an α-halogenated acyl. Thus, ethyl chloracetyl-α-aminopropionate (chloracetylalanine ester) gives methyl diketopiperazine,



$$ClCH_2CONHCH(CH_3)COOC_2H_5 + 2NH_3 \rightarrow NH\left\langle\begin{matrix}CH_2CO\\COCH(CH_3)\end{matrix}\right\rangle NH + NH_4Cl + C_2H_6O.$$

This method is widely applicable and of great practical importance.

These diketopiperazines are converted into dipeptides when hydrolyzed by means of hydrochloric acid or alkali, the latter being preferable and, indeed, essential in the case of the more complicated members of the series.

(*II*) *Synthesis of Polypeptides by Means of Esters.*—This promises to be of considerable use in the production of complicated compounds ; the nature of the reaction is shown by the production of the methyl ester of hexapeptide from the methyl ester of diglycylglycine :

$$2NH_2CH_2CONHCH_2CONHCH_2COOCH_3 \rightarrow NH_2CH_2CO(NHCH_2CO)_4NHCH_2COOCH_3 + CH_4O.$$

(*III*) *Synthesis of Polypeptides by Halogen Acyl Derivatives.*—A halogen acyl is introduced into an amino acid and the product, or its ester, treated with ammonia :

$$ClCH_2CONHCH_2COOH + 2NH_3 \rightarrow NH_2CH_2CONHCH_2COOH + NH_4Cl.$$

The glycylglycine thus obtained may be again treated with a halogen acyl chloride and the process repeated ; this has already led to the production of pentapeptides and there is, as yet, no sign of any limit being reached. A little consideration will show the enormous number of compounds which are rendered accessible by this method.

(*IV.*) *Synthesis af Polypeptides by Linkage to the Carboxyl Group.*—In its results this may be regarded as an extension of the preceding method. Halogen acyl amino acids are treated with phosphorus pentachloride, in acetyl chloride solution ; the resulting acid chloride readily reacts with the esters of amino acids or with polypeptides ; the product is hydrolyzed and treated with ammonia and a new polypeptide obtained. Thus, α-bromisocaproylglycine (isobutyl δ-bromacetylglycine) with ethyl aminoacetate gives, finally, leucylglycylglycine :

$$C_4H_9CHBrCONHCH_2COOH \rightarrow C_4H_9CHBrCONHCH_2COCl \rightarrow C_4H_9CHBr(CONHCH_2)_2CO_2C_2H_5 \rightarrow C_4H_9CH(NH_2)(CONHCH_2)_2COOH.$$

This method is also capable of wide application.

Natural proteids and their decomposition products, such as albumoses, peptones, etc., are all optically active, therefore the synthesis of optically active polypeptides is a matter of considerable importance and interest. Of various methods which have been tried, the one which appears to be of the most general utility is by the use of the chlorides of active amino acids (*vide* p. 540).

Up to the present time about 70 polypeptides have been synthesized; the most complicated is the hepta derivative, leucylpentaglycylglycine.

The structure of polypeptides and of diketopiperazines is anything but a simple matter. To prove that they consist of amino acids with amide linkages by no means exhausts the subject, as shown by the fact that there exists no method for distinguishing between the following 4 formulæ for glycylglycine:

$$H_2NCH_2CONHCH_2COOH\ ;$$

$$H_3\underline{NCH_2CONHCH_2COO}\ ;$$

$$H_2NCH_2C(OH):NCH_2COOH\ ;$$

$$H_3\underline{NCH_2C(OH):NCH_2COO}.$$

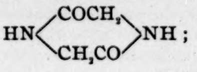
For the sake of simplicity, the first formula has been assumed in all the work that has been published up to the present. The possible complications of structure are, of course, greater in the case of the aminodicarboxylic and the diamino acids.

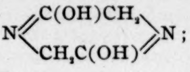
A peculiar kind of isomerism has been observed with some compounds, thus glycylglycinecarboxylic acid,

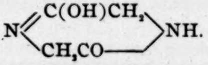
$$HO_2CNHCH_2CONHCH_2CO_2H,$$

yields 2 *neutral* esters.

Finally, it may be pointed out that 2,5-diketopiperazine itself may have 3 possible structures, represented by the formulæ:







A most interesting discussion of the configuration of polypeptides and of the 2,5-diketopiperazines is given in the lecture, but space will not permit of its reproduction; it will suffice to say that the new compounds offer an unparalleled wealth of material for testing the general theory of optically active carbon compounds; hitherto the results which have been obtained are in strict agreement with the current theory.

The second part of the lecture concludes with an account of the general properties and reactions of polypeptides; allusion to the more important of these has been made in the foregoing pages.

Fischer devotes the third part of his lecture to the proteids, and gives first a rather full description of his "ester method" for the separation of the products of acid hydrolysis. Briefly, this consists in hydrolyzing the proteid with hydrochloric acid and esterifying the highly concentrated product by means of alcohol and hydrogen chloride, the resulting esters being separated, first by distillation under greatly reduced pressure, then by special methods which have been referred to in the earlier pages of this report. Detailed directions are given for the isolation and identification of the more frequently occurring monamino acids.

The most important result of the employment of the ester method has been the comparatively easy isolation, from the hydrolysis products of proteids, of constituents which had previously been overlooked, or which could only be separated when they were present in relatively large quantity. A list is given of 21 proteids which have been investigated in this manner by Fischer and his students. He has also examined the products of the action of ferments, such as pepsin and pancreatin, on proteids and has investigated the substances obtained by the hydrolysis of casein by means of potassium hydroxide.

In considering the constitution of the proteids, the question has been raised as to whether the amino acids which result from their fermentative decomposition are preformed in the molecule; Fischer is firmly of the opinion that they are.

His work on the peptones and albumoses, so far as it has progressed, shows that the substances formed by their resolution are essentially similar to those from the proteids, other chemists who have investigated this subject and who have obtained somewhat different results, have always attempted to separate their products by precipitation, a method which is quite inadequate.

Regarding the structure of the proteids but little can be said; undoubtedly the connection of the amino acids with the proteid molecule is by an amide linkage, but to admit this is far from exhausting the possibilities; probably there are piperazine rings, which are known to open very easily, while the hydroxyl groups of the hydroxyamino acids undoubtedly play an important part in the structure and reactivity of the proteids.

Kossel's suggestion that *all* albuminoid compounds contain a "protamine nucelus" is hardly supported by the general results of Fischer's work.

It is abundantly evident that the territory which Fischer has entered will require, for its comparatively complete exploitation, the combined labor of numerous chemists extending over many years, and that it will involve the preparation of an enormous number of new compounds, the question arises, therefore—Will the results be likely to justify this expenditure of time, money and energy? Perhaps the most important effect of such researches will be that the experience and knowledge gained in the investigation of the synthetical compounds, may permit of the isolation and artificial preparation of the constituents of natural peptones and albumoses, in a manner similar to the production of glycine-*d*-alanine anhydride from silk, which is the first example of such a result. This phase of the work alone will involve an enormous amount of work, on account of the varied composition of the different proteids. The synthetical production of the true albumins is a problem of very much greater difficulty and, for its solution, entirely new methods of attack will have to be discovered. Even when this has been accomplished the further question will arise as to the value of the results to biology. Undoubtedly their worth will depend on the method of synthesis employed. Should the production of the new compound depend on a mere accident, such, for example, as the production of a proteid identical with one found in nature, by fusing an amino acid with a dehydrating agent, the result would be of but little value to the chemistry of the albumins and of practically none to biology. The slower method, however, attended with a thorough exploration of the properties of the individual compounds, should go far to clear up the behavior of proteids, ferments, toxins, etc. J. Bishop Tingle.

REVIEWS.

Conversations on Chemistry. First Steps in Chemistry. By W. Ostwald, Professor of Chemistry in the University of Leipzig. Authorized translation by Stuart K. Turnbull. Part II.: The Chemistry of the Most Important Elements and Compounds. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall. 1906. Price, $2.00.

The first volume of this book, treating of general chemistry, was recently reviewed in this Journal.[1] In the present volume Ostwald talks of the elements and their compounds, of acids and bases, of combining weights and gaseous volumes, as well as of atoms and molecules and of electrolytes. These and other matters are fully, admirably and luminously treated—from his point of view.

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[1] This Journal, 34, 255.

Teachers of chemistry who realize how difficult it is to present chemical fact and theory, in the lecture room or laboratory, in a really clear and simple way, will do well to read this book with close attention ; it is profitable to study the author's methods of presentation, and especially profitable when his method differs essentially from that in common use. His explanation of the atomic theory and of gaseous volumes is particularly interesting and clever. To quote a few sentences, referring to the law of combining weights :

Master—" What then requires explanation in this law ?"

Pupil—" Really nothing ; but I thought there might perhaps be something especial in the background behind such a remarkable law."

M.—" Just so ! Of course this is quite a childish idea like that of the peasant who, when they tried to explain the locomotive to him, said : 'I understand all that very well ; but then, where really is the horse which drags all these wagons ?' "

P.—" Ha, ha, ha ! He was stupid !"

M.—" Not so very. He had no experience of the fact that we can set a wagon in motion otherwise than with a horse yoked on in front, and therefore he supposed that he would be able to understand the locomotive only after they had showed him the hidden horse. In point of fact, chemists have, for the last hundred years, assumed that there is such a hidden horse in the law of combining weights."

P.—" A horse ! What does that mean ?"

M.—" I speak figuratively. I mean that formerly it was necessary just in the same way for people to assume some such cause as regards the law of combining weights ; because without it they could not put into expression the existence of such a law,—just as the peasant could not express to himself the idea that a train can get in motion without a horse."

P.—" Then what does the chemical horse look like ?"

M.—" You know already ; it is the atom."

What the master says is always well put, but the objectionable pupil is always " butting in," as he would say were he an American pupil. The author should rewrite the book and eliminate him, for he has no semblance of a live boy, but is an automaton, wound up to put the desired question at the proper moment, to be preternaturally acute when this acuteness acts as a foil to the thickheadedness of " other chemists," to be preternaturally dull when especial emphasis and repetition is desired, and to throw in a slang expression, or would-be naive remark every few pages.

While the function of the pupil was doubtless suggested by Socratic dialogue, his actual performance is largely that of Jules Verne's comic Frenchman. Readers of Jules Verne will recognize that his different books are made—in the literary sense—by one receipt; among the ingredients are the scientific man, who doles out the science which justifies the trip to the moon or elsewhere, or whiles away the time en route, and the comic Frenchman, whose function is to enliven the science of the scientific man by jokes and gambols; and this is often the function of the pupil; in Ostwald's words, he is to render the book "penetrating and lively."

In the review of the first volume the reviewer attempted to thus benefit his review by quoting the pupil's quips. On the same principle he ventures to enliven the close of the present review by the merry jest which lies in the last words of the master:

P.—"Tell me could I not get some book to read as a preparation for my future studies?"

M.—"I see; your talk about preparation is merely an excuse to find out what lies beyond. However I have no objections to make; self-chosen work usually gives not only more pleasure, but better results than a set task. At the present day we are rather awkwardly situated as regards chemical text-books. During the last 15 years a great change has sprung up in our views and acceptance of science, and most of our literature is written in accordance with earlier ideas. I have directed your studies along the lines of modern thought, and to unlearn them by changing to the old style would cause you a great deal of unnecessary difficulty. So there is really only one book I can recommend to you as being quite up to date; it is 'Outlines of General Chemistry,' by W. Ostwald. The subject matter is more difficult than what you have been accustomed to; but it will answer many of the questions whose explanations I have, so far, had to reserve."

P.—"That is just the book I want."

Oh, Disciples of the Master! Bearers of light into dark places! Preachers and Publishers of the Word to "other chemists!" Is *this* your reward? E. R.

CHEMIE DER ALICYKLISCHEN VERBINDUNGEN. Von OSSIAN ASCHAN, A. O. Professor an der Universität Helsingfors. Braunschweig: Fr. Vieweg und Sohn. 1905. pp. xlvi + 1164. Price, M. 40.

This admirable work, which is dedicated to Professor von

Baeyer, in celebration of his seventieth birthday, was planned as the result of the author's labors on the last German edition of the organic portions of Roscoe and Schorlemmer's "Treatise." The scope and nature of the book can best be shown by an abstract of the table of contents. The general part (I.) comprises 386 pages, divided as follows: Introductory, pp. 7; Theoretical development of the chemistry of alicyclic compounds, pp. 228, divided into 12 chapters; Influence of ring formation on the chemical nature of alicyclic compounds, pp. 26, 2 chapters; Influence of ring formation on the physical properties of alicyclic compounds, pp. 65; The stereochemistry of alicyclic compounds, pp. 60, 4 chapters. The special part (II.) of 778 pages, is devoted to the Methods of formation and preparation of the alicyclic compounds, arranged systematically, pp. 39, 10 chapters; Monocyclic compounds, pp. 459, 6 chapters; Bicyclic compounds, pp. 213, 6 chapters; Tri- and Polycyclic compounds, pp. 36. The index, pp. 30, is admirably full. Only an extensive use of the book can show how far it has been possible to exclude errors; at the most they can but be of a trifling nature.

The plan of writing monographs on special branches of chemistry is an entirely good one, especially if the author is an acknowledged authority on the subject, as in the present case, but, for complete success, it is necessary that the collection of material should be as exhaustive as possible and that it should be clearly and systematically arranged, the style should be attractive and, wherever it can be done, the gaps in our present knowledge of the subject should be indicated and fresh lines of research suggested. Judged by all these criteria, the volume under review is an unqualified success; the author's name is a thorough guarantee of his competency for the work, and the brief synopsis given above shows how completely the subject has been covered and how admirably the material has been arranged. As an indication of the amount of labor involved, it may be mentioned that the book includes more than 5,000 citations, which are brought down to August, 1905. The style of the book is most pleasing—there is nothing of the "dry-as-dust" order about it. The first 12 chapters, dealing with the general theory of alicyclic compounds, treat the subject historically and are extremely fascinating reading. The author points out the urgent need for more work on the physical properties of these compounds, in many cases no data whatever are available, and frequently the statements in the literature are incorrect and contradictory. In other parts of the book, too, lines of fruitful inquiry are indicated. This volume may serve as a model of what such a work should be; the author has placed his fellow-chemists under a debt of gratitude by producing it, and he is to be warmly congratulated on its successful completion.

J. B. T.

DIE ELEKTROLYSE GESCHMOLZENER SALZE. Zweiter Teil: Das Gesetz von Faraday; Die Überführung und Wanderung der Ionen; Das Leitvermögen. Von RICHARD LORENZ., Dr. phil., o. Professor für elektrochemie und physikalische Chemie am eidg. Polytechnikum in Zurich. Mit 59 in den Text gedruckten abbildungen. Halle a. S.: Druck and verlag von Wilhelm Knapp. 1905. pp. 257. Price, M. 8.

This book, which is Volume 21 of the "Monographs on Applied Electrochemistry," deals with a subject which is somewhat removed from the ordinary—the electrolysis of fused salts. It has long been known that, at elevated temperatures, dissociation into ions takes place, and that fused salts conduct the current. The literature on this subject has, until the present, been rather widely scattered. In this monograph Lorenz has brought together, in a very satisfactory form, what is known on the whole subject.

The larger divisions, under which the subject-matter is classified, are: The Law of Faraday; The Transference and Migration of the Ions; Conductivity.

From this it will be seen that the same general plan is followed as in dealing with the electrolysis of solutions.

The volume in question is a valuable addition to the already valuable series of monographs. H. C. J.

A LABORATORY GUIDE TO THE STUDY OF QUALITATIVE ANALYSIS, Based upon the Application of the Theory of Electrolytic Dissociation and the Law of Mass Action. By E. H. S. BAILEY, PH.D., Professor of Chemistry, and HAMILTON P. CADY, PH.D., Assistant Professor of Chemistry in the University of Kansas. Fifth edition, thoroughly revised. Philadelphia: P. Blakiston's Son & Co. 1905. Price, $1.25 net.

The fourth edition of this book appeared in 1901 and was reviewed in this JOURNAL[1] by Professor H. C. Jones. It will suffice to say here that it is a good laboratory manual, written in accordance with the theory of electrolytic dissociation, treating of the detection and separation of cations and anions, instead of metals and acids, and has, as a positive advantage, the benefit of the explanation offered by physical-chemical theory of certain analytical reactions. E. R.

KURZES LEHRBUCH DER ORGANISCHEN CHEMIE. Von PROF. DR. A. BERNTHSEN. Neunte auflage bearbeitet in Gemeinschaft mit DR. ERNST MOHR. Braunschweig: Fr. Vieweg und Sohn. 1905. pp. xxii + 638. Price, M. 11.

This excellent text-book is so well known that a review of the new edition may be confined to a statement of the changes and improvements which it contains. The text has been thoroughly revised, new matter having been added and certain portions of the old eliminated ; this, in itself, has not involved an increase in the size of the book, the extra number of pages in the present edition being due to the use of large type for certain paragraphs which were formerly set more closely. The most important alteration, however, is in the division of the compound, into three classes, *viz.*, methane derivatives pp. 283, isocyclic derivatives pp. 198, and heterocyclic derivatives pp. 80 ; this arrangement is logical and should be of considerable benefit to the users of the book ; the general introductory portion occupies 40 pages. The author is to be congratulated on these alterations. The production of the ninth edition shows that the work has obtained the recognition and appreciation which it so justly merits. J. B. T.

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[1] THIS JOURNAL, 27, 157.

THE PRODUCTION OF ALUMINUM AND ITS INDUSTRIAL USE. By ADOLPHE MINET, Officer of Public Instruction and Editor of "L'Electrochimie." Translated, with additions, by LEONARD WALDO, S.D. (Harv.). First edition, first thousand. New York : John Wiley & Sons. 1905. pp. 261. Price, $2.50.

Minet's monograph is a fairly complete enumeration and description of the different methods which have been suggested for the production of aluminium, and of the various chemical and industrial uses of the metal from the point of view of a practical inventor with some knowledge of thermo-chemistry ; it is supplemented by a few statistical tables and a brief account, by the translator, concerning the production of aluminium in the United States.

The author gives many details of his own process, which, although it was once in use in France, has been abandoned, but his account of Héroult's or Hall's processes is brief. The former is used in Europe, the latter in Europe and in America.

At the present time the yearly output of aluminium is from 14,000,000 to 18,000,000 lbs., of which more than one-half is made by the Pittsburg Reduction Co., at Niagara Falls. The price is 31–37.5 c. per lb. here and 22 c. in Europe. E. R.

THE CONDUCTIVITY OF LIQUIDS. Methods, Results, Chemical Applications and Theoretical Considerations. By OLIN FREEMAN TOWER, PH.D., Assistant Professor of Chemistry, Western Reserve University. Easton, Pa. : Chemical Publishing Company. 1905. pp. 182. Price, $1.50.

This useful little book contains just such information as one frequently desires to have at hand. About the only fault we can find with it is in the title. Conductivity of *Solutions* and not of "Liquids" would have been more in accordance with the contents.

The author discusses such fundamental subjects as: Methods and Apparatus Used in Determining Conductivity; Dissociation of Electrolytes; Migration of Ions, both relative and absolute values; The Determination of $\mu\infty$; Influence of Temperature and Pressure on Conductivity; Solutions Containing Two Electrolytes; Non-aqueous Solutions and Conductivity of Electrolytes in Mixed Solvents. Useful tables of conductivity data are also appended.

The book is very well written, the style being clear, interesting and attractive. It is unfortunate that the contents could not have been brought a little nearer to the date of publication, but the reason for not doing so is given by the author in his preface.

It is to be hoped that the volume will have the wide circulation it deserves.

H. C. J.

EXPERIMENTAL ELECTROCHEMISTRY. By N. MONROE HOPKINS, PH.D., Assistant Professor of Chemistry in the George Washington University, Washington, D. C. With 130 illustrations. New York: D. Van Nostrand Company. 1905. pp. 284. Price, $3.00 net.

It is stated in the preface that "It has been the aim of the author to produce a book that will prove useful in both the lecture room and the laboratory. Although a work upon the subject of electrochemistry must presuppose a working knowledge of chemistry and electricity, it has been the object of the writer to introduce the subject as clearly as possible, dealing with chemistry and electricity without assuming too much on the part of the student." Again, "Electrochemistry is at best a subject for the advanced student, and in order to carry out the experimental work with profit, as given here, he must have pursued beforehand laboratory courses in both chemistry and physics."

It will be recognized that this is a sound basis upon which to write a book on electrochemistry.

The first part of the book deals with the strictly scientific side of electrochemistry, while the second half has to do with more practical questions, such as the production of nitric acid from the air, the electrolytic production of the metals, the electric furnace and its products, the electrolytic preparation of organic compounds, primary and secondary cells, electricity from carbon, etc.

The style is clear and very readable. A few matters could be revised to advantage. Thus, on page 1, we find "*basic* experimental evidence." On page 48, the term "*molugram*" is certainly not euphonious, and it is to be hoped will not find its way into physical-chemical literature.

The equation on page 108, in connection with the electrolysis of concentrated sulphuric acid, must not be accepted literally, since atomic oxygen is certainly not produced. Further, the use of the term "*heavy*" as applied to current will scarcely meet the demands of the purists.

In connection with the theory of the electrolysis of sulphuric acid, it is not pointed out with sufficient clearness that the older view is unquestionably wrong; and the newer view is not sufficiently elaborated. A few ions are not capable of carrying "many amperes," but many coulombs of electricity.

It will, of course, be recognized that these are minor matters, which can easily be corrected in a new edition.

The work, as a whole, is interesting and contains a number of ingenious experiments, some of which have important new features. It will doubtless find a good demand, especially in laboratories where considerable stress is laid upon electrochemistry. We wish it the success which it deserves.

H. C. J.